

RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXIV

NUMBER 3



July-September, 1951

Published Quarterly under the Auspices of the
DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY
at Prince and Lemon Sts., Lancaster, Pa.

KOSMOS 60 R
KOSMOS 60 R

KOSMOS 60 RF
KOSMOS 60 RF



Kosmos 60 is today the most talked about furnace black for reinforcing natural and synthetic rubber. It originates from oil and is perfected by United's exclusive process. Its superb processing and balance of strength make for the best in rubber products.

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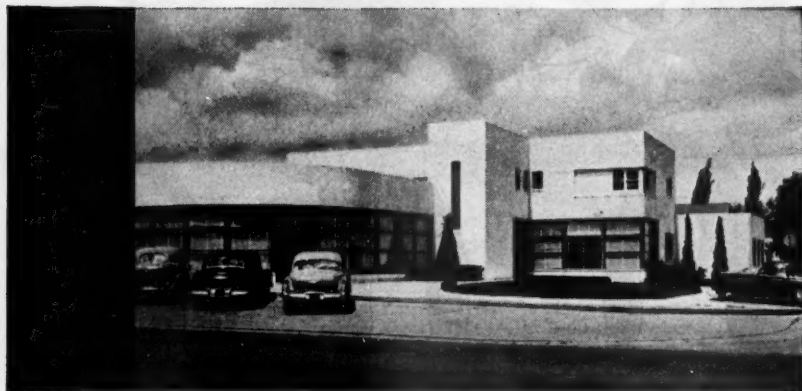
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Meanwhile, if you're in the vicinity, why not pay us a visit? We'll be glad to show you through our new laboratories—which really have to be seen to be fully appreciated.



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Philblack*O and Philblack*A

Remove the nerve the easy way!

You always get smooth, accurate extrusions with Philblack A or Philblack O. Rubber stocks mix promptly . . . without balky nerve difficulties. Furthermore, uncured stocks compounded with the Philblacks possess desirable plasticity, workability and excellent mold flow. When compounding, include either or both of these fast-curing, easy-processing Philblacks.

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Warehouses in Akron, Boston, Chicago and Trenton.

West Coast agent: Harwick Standard Chemical Company, Los Angeles

Canadian agent: H. L. Blachford, Ltd., Montreal and Toronto.



*A Trademark

**DOUBLE-CHECKED ✓ CHEMICALS
FOR THE RUBBER INDUSTRY**

VULTAC

Vulcanizing agent for natural rubber and synthetic elastomers. Vultac eliminates sulfur bloom normally encountered with pigment sulfur, and imparts easy processing characteristics to GR-S formulations.

The uniform vulcanization achieved through the use of the VULTACS results in GR-S and nitrile rubber stocks possessing the following superior qualities:

1. Maintenance of tensile strength and elongation upon extended cure.
2. Retention of tensile strength and elongation after severe aging.
3. Outstanding resistance to heat.
4. Outstanding resistance to flex cracking and tear, before and after aging and at elevated temperatures.

	VULTAC No. 2	VULTAC No. 3
Type Alkylphenol Sulfide	Disulfide	Disulfide
Sulfur Content	23%	28%
Color and Form	Hard Brown Resin	Hard Brown Resin
Softening Point (ASTM E28-36T)	55-65°C.	70-80°C.
Solubility	Readily soluble in all common organic solvents except the alcohols.	Readily soluble in all common organic solvents except the alcohols.
Specific Gravity 25/25°C.	1.16-1.17	1.19-1.20
Approx. Lbs. per Gallon	9.7	10.0

**25th
Anniversary**

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TYPE A — for stocks requiring unsurpassed solvent resistance.

TYPE FA — for extruded goods that must withstand aromatic blended fuels and permanent oil and weather-resistant putties.

TYPE PR-1 — for molded goods that must withstand aromatic blended fuels.

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WATER DISPERSIONS:

MX & WD-6 — for liquid compounds to give films of high solvent and moisture resistance.

MF — for liquid compounds to give films of good solvent and low temperature resistance.

WD-2 — For liquid compounds to give films which must be free from odor. Films also have excellent low temperature resistance.

PLASTICIZERS:

TP-90B — for plasticizing natural rubber, GR-S, Buna N and GR-M for extreme low temperature resistance.

TP-95 — for plasticizing Buna N rubbers, GR-M and vinyl resins for excellent low temperature resistance and good heat resistance.

LIQUID POLYMERS:

LP-2 — A liquid polymer of 100% solids which vulcanizes to a tough resilient solid without shrinkage when mixed with curing agents.

LP-3 — same as LP-2 but of a lower viscosity.

TACKIFIERS:

GALEX W-100 & W-100D — A non-oxidizing rosin for imparting tack to the Buna rubbers. Also valuable in GR-M compounds.

TECHNICAL INFORMATION
AND SAMPLES ON REQUEST

Thiokol
CORPORATION

781 NORTH CLINTON AVENUE
TRENTON • NEW JERSEY

^{*}THIOKOL, REG. U.S. PAT. OFF.

40-50 degrees higher
heat distortion point in

Plio-Tuf

— made with new PLIOLITE S-6C

Now you can get all the advantages of PLIO-TUF — impact resistance, hardness, rigidity, chemical resistance, water resistance, machinability, good electrical properties — PLUS greatly improved resistance to distortion by heat. Thanks to a new Goodyear-developed resin—called PLIOLITE S-6C — you're assured of heat distortion points from 40° to 50° higher.

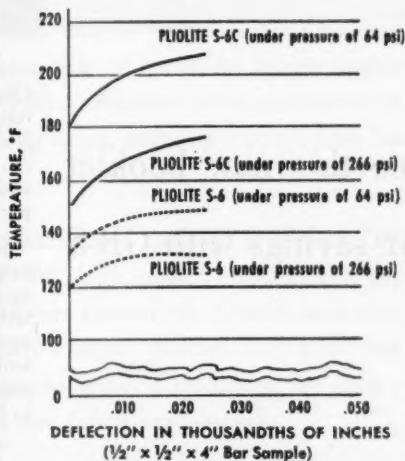
New temperature ranges in the 190°-200° F. range give you higher heat resistance in the finished item, and let your finished molded products cope with a wider range of operating conditions—yet with no sacrifice to the outstanding physical properties of PLIO-TUF.

PLIO-TUF is a use-proved combination of resin and rubber—already in full use by makers of such diverse items as helmets, textile spools, golf ball covers, carrying cases, bowling pin

covers, chemical buckets and a wide range of molded items. For help in fitting PLIO-TUF into your present or future plans—samples for your evaluation — full details about this outstanding production material, write to:

Goodyear, Chemical Division
Akron 16, Ohio

Comparison of Heat Distortion Temperatures
PLIOLITE S-6 vs PLIOLITE S-6C



HIGHER HEAT DISTORTION POINT than with any other high styrene butadiene copolymer is shown in tests of PLIOLITE S-6C on Tinius-Olsen Heat Distortion Tester. Chart compares results of similar tests on PLIOLITE S-6.

Plio-Tuf, Pliolite-T.M.'s The Goodyear Tire & Rubber Company, Akron, Ohio



This resin available in
experimental quantities only

GOOD YEAR



See this new booklet
for savings with GR-S

Chances are you've got GR-S on your mind. Well, that's what this new booklet is all about. It's titled "Purecal in GR-S" . . . it's a complete discussion of Purecal* and other non-black fillers in GR-S, compared with carbon blacks.

It gives you the facts on a new GR-S base compound of carbon black quality that can be made with Purecal. And it tells the story of the advantages of this new compound. This booklet is a working tool that offers basic information on the compounding and processing of Purecals in GR-S and cold rubber.

"Purecal in GR-S" is hot off the press and it wouldn't be a bad idea to write for your copy soon.

* Trade Mark

Soda Ash • Caustic Soda • Bicarbonate of Soda
Calcium Carbonate • Calcium Chloride • Chlorine
Hydrogen • Dry Ice • Synthetic Detergents
Glycols • Carbose (Sodium CMC) • Ethylene
Dichloride • Propylene Dichloride • Aromatic
Sulfonic Acid Derivatives • Other Organic
and Inorganic Chemicals

WYANDOTTE CHEMICALS CORPORATION
Wyandotte, Michigan • Offices in Principal Cities



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REG. U. S. PAT. OFF.



... a winner

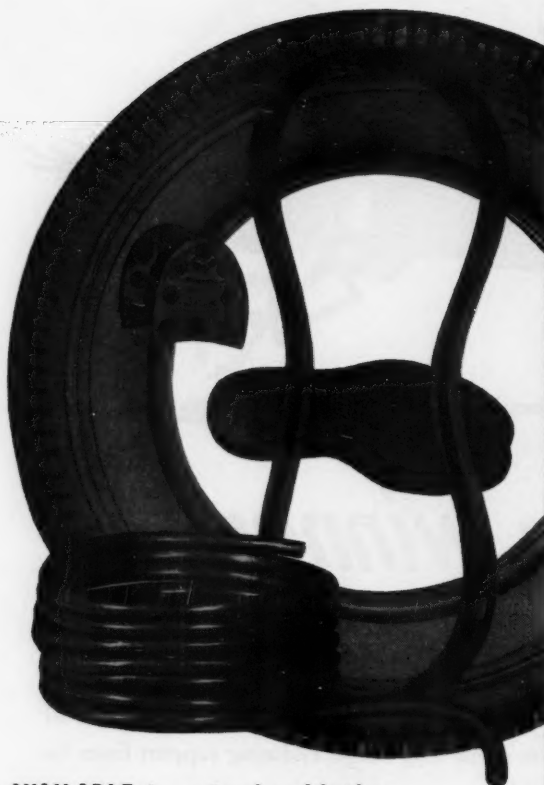
To win in a long race the Indian requires the continuing co-operation of his pony. In the highly competitive rubber industry the manufacturer of tires needs long range, enduring support from his suppliers.

Users of Sid Richardson Carbon Co. **TEXAS "E"** and **TEXAS "M"** high quality, economical-to-use channel blacks are assured this type of assistance. With the world's largest channel black plant and abundant, nearby natural resources, we assure your present and future requirements.



Sid Richardson
C A R B O N C O.
FORT WORTH, TEXAS

GENERAL SALES OFFICES
EVANS SAVINGS AND LOAN BUILDING
AKRON 8, OHIO



AVAILABLE to retard oxidation and flex cracking

Monsanto has available for immediate delivery three products with proved-in-service efficiency for retarding oxidation and flex cracking in such products as shoe soles and heels, tires, cable jackets and mechanicals. All of these antioxidants are effective in synthetic rubber, in natural rubber, in reclaimed rubber.

SANTOFLEX B — 1.0 to 2.0% of Santoflex B gives excellent results in retarding flex cracking and oxidation; 3.0 to 4.0% gives high resistance to weathering and flexing.

SANTOFLEX BX — A preferred antioxidant for retarding oxidation and flex cracking. It mildly activates accelerators of the thiazole type. Use not over 2.0% to avoid blooming.

SANTOFLEX 35 — The choice of many manufacturers for retarding oxidation and flex cracking. It mildly activates thiazole-type accelerators. Blooming can be avoided by using not over 1%.

For technical information on these and other Monsanto Chemicals for the Rubber Industry, contact MONSANTO CHEMICAL COMPANY, Rubber Service Department, 920 Brown Street, Akron 11, Ohio.

MONSANTO CHEMICALS FOR THE RUBBER INDUSTRY

ANTIOXIDANTS

Flectol* H
Santoflex* B
Santoflex BX
Santoflex 35
Santoflex AW
Santowhite* Crystals
Santowhite MK
Santowhite L

ALDEHYDE AMINE ACCELERATORS

A-32
A-77*
A-100

MERCAPTO ACCELERATORS

Santocure*
El-Sixty*
Ureka* C
Ureka Base
Mertax (Purified Thiotax)
Thiotax (2-Mercapto benzothiazole)
Thiofide* (2,2' dithio-bis
benzothiazole)

GUANIDINE ACCELERATORS

Diphenyl Guanidine (D.P.G.)
Gualtal*

ULTRA ACCELERATORS FOR LATEX, ETC.

R-2 Crystals
Pip-Pip
Thiurad* (Tetra methyl thiuram
disulfide)
Ethyl Thiurad (Tetra ethyl thiuram
disulfide)
Mono Thiurad (Tetra methyl
thiuram mono sulfide)
Methasan* (Zinc salt of dimethyl
dithiocarbamic acid)
Ethasan* (Zinc salt of diethyl
dithiocarbamic acid)
Butasan* (Zinc salt of dibutyl
dithiocarbamic acid)

WETTING AGENTS AND DETERGENTS

Areskap* 50
Aresklene* 375
Santomerse* S
Santomerse D

SPECIAL MATERIALS

Thiocarbaniide ("A-1")
Santovar*-A
Santovar-O
Insoluble Sulfur "60"
Retarder ASA

COLORS

REODORANTS

*Reg. U. S. Pat. Off.



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BLACKS**

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A LOW COST BUNA N PLASTICIZER

Excellent for

**LIGHT COLORED
PRODUCTS**

PANAFLEX BN-1

PANAFLEX BN-1 is an economical, light-colored plasticizer for synthetic rubber — especially butadiene-acrylonitrile type.

This hydrocarbon plasticizer completely replaces dibutyl phthalate in nitrile rubbers—produces soft vulcanizates having high tensile, excellent elongation, and very low modulus. **PANAFLEX BN-1** plasticized stocks possess good ageing properties, superior electrical characteristics, and show good gasoline and oil resistance.



PAN AMERICAN
DIVISION *Chemicals*
Pan American Refining Corp.

122 EAST 42nd STREET

Plant

Texas City, Texas

NEW YORK 17, N. Y.

chemicals for the rubber industry

ACCELERATORS

Thiazoles

MBT (Mercaptobenzothiazole)

MBTS (Benzothiazyl disulfide)

Guanidine

DPG (Diphenylguanidine)

DOTG (Diorthotolylguanidine)

Accelerator 49

ACTIVATOR

Aero* AC 50

ANTIOXIDANT

Antioxidant 2246

(Non-staining, non-discoloring type)

PEPTIZER

Pepton® 22

RETARDER

Calco Retarder P.D.

STIFFENING AGENT

Calco S.A.

SULFUR

Rubber Maker's Grade

*Trade-mark



AMERICAN Cyanamid COMPANY

CALCO CHEMICAL DIVISION
INTERMEDIATE & RUBBER CHEMICALS DEPARTMENT
BOUND BROOK, NEW JERSEY, U.S.A.

***To the
Rubber Industry! ~ ~ ~***

This Journal is supported by advertising from leading suppliers to the industry. More advertising will permit the publication of a greater number of important technical papers on rubber which will make RUBBER CHEMISTRY AND TECHNOLOGY even more valuable as a convenient reference of "Rubberana."

Specify materials from suppliers listed on page 32. Urge other suppliers to advertise in

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Advertising rates and information about available locations may be obtained from E. H. Krismann, Advertising Manager, Rubber Chemistry and Technology, c/o E. I. du Pont de Nemours & Company, 40 E. Buchtel Ave. at High Street, Akron 8, Ohio.

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DU PONT RR-10

a new reclaiming agent

If you're producing reclaim, it will pay you to investigate RR-10, Du Pont's new reclaiming agent. After extensive experimentation and plant trials, many companies have found it to be the most effective agent ever tried for reclaiming rubber, GR-S, and mixtures of these elastomers. They report that RR-10 produces smooth reclaims with good tack . . . that it does the work quickly and economically. One user states, "RR-10 is the most powerful reclaiming agent we have ever tried."

The use of RR-10 results in higher-quality reclaim because less reclaiming oils are necessary. It can be used in either the pan or neutral (zinc chloride) process. And unlike most other chemical reclaiming agents, it is also effective in the alkali process.

Samples of Du Pont RR-10 are available. For complete information, contact our nearest branch office. E. I. du Pont de Nemours & Co. (Inc.), Rubber Chemicals Division, Wilmington 98, Delaware.

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Los Angeles, Cal.	845 E. 60th St.	ADams 3-5206
New York, N. Y.	40 Worth St.	COrtlandt 7-3966

DU PONT RUBBER CHEMICALS

E. I. du Pont de Nemours & Co. (Inc.), Wilmington 98, Del.



BETTER THINGS FOR BETTER LIVING...THROUGH CHEMISTRY

CIRCOSOL-2XH OFFERS 5 ADVANTAGES AS ELASTICATOR FOR GR-S... REGULAR AND COLD

Increased use of synthetic rubber makes the unique elasticator
Circosol-2XH increasingly important to compounders

1. SPECIALLY REFINED FOR RUBBER-PROCESSING

Circosol-2XH is not an ordinary mineral oil. It's a petroleum-base process aid, refined within rigid specifications solely to meet the exacting requirements of rubber compounders. The product is a heavy viscous liquid, clear, transparent, and with a pale green color as observed by transmitted light. It is composed of hydrocarbons of comparatively high molecular weight entirely derived from selected crude petroleums. Its low volatility precludes any fuming and losses during mixing in the banbury and processing on the mills.

2. ASSURES PRODUCT UNIFORMITY

Circosol-2XH is refined under precision-controlled conditions permitting no deviation from specifications. It minimizes the danger of product variation. To quote the technical superintendent of a large rubber company: "With Circosol-2XH you never have to worry about results being different."

3. HIGH NAPHTHENICITY

Leading rubber technologists are unanimous in agreeing that hydrocarbons with a high degree of naphthenicity are best suited for processing and plasticizing rubber. Sun's exclusive refining process retains the high naphthenicity of the selected crudes from which Circosol-2XH is derived.

4. CAN BE USED WITH ALL COLORS

Unlike products offered in competition with it, Circosol-2XH is a light-colored

compound. It can therefore be used in such items as white footwear, hospital sheeting, white seals and gaskets.

5. GIVES GR-S EXTRA RESILIENCE

Circosol-2XH improves the rebound so necessary for many uses. Furthermore, heat build-up is low—in tire tread extrusion, for example.

TYPICAL COLD RUBBER TREAD COMPOUND USING CIRCOSOL-2XH

GR-S-478	100.00
ZnO	3.00
HAF BLACK	50.00
FLEXAMINE	1.25
STEARIC ACID	2.00
SULFUR	1.80
SANTOCURE	1.25
CIRCOSOL-2XH	10.00

PHYSICAL PROPERTIES (60' cure @ 292 F)

TENSILE, psi	3455
MODULUS (300%), psi	1775
ELONGATION, %	505
SHORE A HARDNESS	59
REBOUND (Goodyear-Healy), Room Temp.	57
HEAT BUILD-UP (Goodrich), deg. Fahr.	68

SUN INDUSTRIAL PRODUCTS

SUN OIL COMPANY, PHILADELPHIA 3, PA. • SUN OIL COMPANY, LTD., TORONTO AND MONTREAL



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Published under the Auspices of the
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CARBON BLACKS

for RUBBER COMPOUNDING

MPC (Medium Processing Channel)
STANDARD MICRONEX

EPC (Easy Processing Channel)
MICRONEX W-6

HAF (High Abrasion Furnace)
STATEX-R

FF (Fine Furnace)
STATEX-B

FEF (Fast Extruding Furnace)
STATEX-M

HMF (High Modulus Furnace)
STATEX-93

SRF (Semi-Reinforcing Furnace)
FURNEX

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REGISTRAR
G. E. HOLMES-SIEDLE.

To Members of the American Chemical Society.

DEAR SIR,

It is my pleasant duty to send you brief particulars of the Institution and a cordial invitation to Membership.

As a result of the many enquiries received from delegates to the Cleveland Conference and others in the United States for an opportunity to take part in the activities of the Institution and to receive its literature, my Council has agreed, with the courteous aid of the Division of Rubber Chemistry, to issue this special invitation to Membership to our friends in North America.

Very truly yours,

G. E. Holmes-Siedle

Registrar.

The Institution

FOUNDATION

The Rubber Industry owes its development largely to scientific and technical research and the Institution was founded in 1921 to foster scientific and technical advancement and to disseminate the results.

OBJECTS

The main objects for which the Institution is established are:—

1. To promote the development of rubber science and technology, record invention and recognise merit.
2. To maintain a Diploma as a means of recognising and raising the status of those working in the Rubber Industry.
Fellowship of the Institution (F.I.R.I.) is awarded to eminent members of the Industry without examination: Associateship (A.I.R.I.) and Licentiatehip (L.I.R.I.) are awarded by examination.
3. To encourage and widen the scope of technical education, thus securing well trained chemists, technologists and operatives to carry on, enlarge and preserve the Rubber Industry.
4. To promote the dissemination of the knowledge of rubber science and technology by the holding of meetings and the publication of the "Transactions" and other literature.
5. To provide a means of association between persons interested in the wider aspects connected with all sections of the Industry including the production, investigation, manufacture and applications of rubber.

PUBLICATIONS

The Transactions I.R.I.: A bi-monthly record of scientific and technological investigations in the realm of rubber and its allied industries: issued to all members.

The Annual Report On the Progress of Rubber Technology: containing systematic accounts of the developments in rubber technology from year to year.

Proceedings: Records of International Conferences organised by The Institution (1938, 1948).

Monographs: Practical technological discussions of manufacturing problems connected with the rubber industry. The first of a series will shortly be published.

MEMBERSHIP

The Institution is international in character and its membership embraces many of the world's leading rubber technologists, scientists and executives. Many important rubber manufacturing companies, together with their technical staffs and executives, are active members and supporters of the Institution.

ORDINARY MEMBERSHIP:—

Ordinary members are entitled to vote at General Meetings of the Institution: to nomination for election to the Council: to receive the *Transactions* and to apply for admission to the Licentiate and Associateship under the Regulations for the Diplomas.

Annual Subscription \$7.50

MANUFACTURING MEMBERSHIP:—

The following are eligible for membership under this heading:—

(a) Manufacturers of rubber products or producers of natural and synthetic rubbers and rubber-like materials, whether corporations or firms.

(b) Manufacturers or suppliers of raw and other materials, plant, machinery, instruments and the like used in the rubber and allied industries, whether corporations or firms.

Annual Subscription \$45.00

MERCHANT MEMBERSHIP:—

Open to corporations or firms directly connected with the rubber and allied industries but not eligible as manufacturing members.

Annual Subscription \$21.00

Manufacturing and Merchant subscribers may appoint one representative who will have the full rights and privileges of ordinary membership.

Application Form Overleaf.

Application for ELECTION as ORDINARY Member. No. A

Received

Institution of the



Rubber Industry

12, Whitehall, London, S.W.1, England.

Name in full

Address

Date of Birth

Nationality

Academic Degrees, Diplomas and Titles (if any)

Statement of Experience in Rubber and Allied Industries

I, the undersigned, on my election to Ordinary Membership of the Institution of the Rubber Industry, undertake to do my utmost to promote the well-being and further the objects of the Institution. I enclose a crossed draft for \$7.50 made payable to "The Institution of the Rubber Industry" covering my subscription for the current year.

Signature of Candidate

Dated this day of

W. Heffer & Sons Ltd., Cambridge, England.

RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Division of Rubber Chemistry
of the American Chemical Society,
Prince and Lemon Streets,
Lancaster, Pa.

Editor.....C. C. DAVIS
Advertising Manager.....E. H. KRISMANN
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NEW BOOKS AND OTHER PUBLICATIONS

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1949. (Vol. XIII). Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W.1, England. $7\frac{1}{4} \times 9\frac{1}{4}$ in., 94 pp. Price: To members, 4/6; To Non-Members, 12/6.—Although somewhat smaller in size than the previous edition (94 pages as compared with 104 pages), this latest review number again lives up to expectations in furnishing data on developments in all branches of the rubber industry which occurred in the year of 1949. Like previous editions, specially contributed sections cover developments in planting, physics and chemistry, synthetic rubber, compounding ingredients, fibers and fabrics, belting, tires, surgical goods, cellular rubber, machinery and appliances, etc. As usual, the lead-off section is a review of history and statistics. These reviews, which include extensive references at the end of each section, furnish an invaluable clue to rubber developments. A carefully cross-referenced subject index is again included. [From the *Rubber Age* of New York.]

AN INTRODUCTION TO THE CHEMISTRY OF THE SILICONES. Second edition. By Eugene G. Rochow. John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. Cloth, 6×9 inches, 213 pages. Price, \$5.00.—In his critical survey of the field, Dr. Rochow reviews the silanes and their derivatives and emphasizes the commercially important silicone polymers. In addition to giving methods for their preparation, their chemical and physical properties, and their uses, he investigates the possibilities of large scale production and covers the various methods of analysis. To bring the new edition up to date, the author has included new material on the carbon-silicon bond, the synthesis of organosilicon compounds, and the physical chemistry of silicones. Enlarged tables of physical properties of organosilicon compounds are included.

PHYSICO-CHIMIE DU LATEX. W. Kopaczewski. Dunod, 92 Rue Bonaparte (VI), Paris, France. 1951. Paper, $6\frac{1}{2} \times 10$ inches, 169 pages.—No systematic research work has yet been carried out on the colloidal equilibrium of latex, and hardly anything is known about the mechanism of the physical or chemical factors capable of disturbing this equilibrium, the author points out in his foreword. For eight years he has studied various latexes, more particularly that of *Euphorbia resinifera*, to determine their physicochemical characteristics, and results have been compared with existing fragmentary knowledge and collected in this monograph, which the author claims is the first attempt at a physicochemistry of latex. The book also includes hitherto unpublished personal researches. It is divided into three parts, discussing generalities, conditions of stability, and analogies. The first part has two chapters. The first briefly discusses the latex-bearing individuals of no fewer than 20 families of plants; the second chapter takes up the physical and colloidal characteristics of latex. Of the three chapters in Part two, the first treats of the phenomena of gelling and gels (the author includes coagulation and coagula) and the physical, mechanical, and chemical agents used in gelling; the second chapter deals with the phenomena, experimental conditions, and mechanism of disjunction (separation into phases or fractions); the third chapter covers stabilization. In Part three, plastomers and elastomers are treated, and finally simple and complex biocolloids. An extensive bibliography concludes the work, which, however, contains no reference notes nor indexes. [From the *India Rubber World*.]

ASTM MANUAL ON QUALITY CONTROL OF MATERIALS. Special Technical Publication 15-C. American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa. 140 pages. Price, \$1.75.—This new manual has been prepared by Committee E-11 on Quality Control of Materials to replace the previously issued "ASTM Manual on Presentation of Data". The new booklet is organized in three parts: (1) presentation of data, representing a revision of the manual being replaced; (2) limits of uncertainty of an observed average, representing a revision of Supplement A in the old manual; and (3) control chart method of analysis and presentation of data, with applicable formulas, tables, and examples. [From the *India Rubber World*.]

THE RUBBER FORMULARY. Edited by Kathleen S. Rostler. Published annually by The Rubber Formulary, P.O. Box 1568, Bakersfield, California. \$85 per year on subscription basis. The Rubber Formulary is a system of recording data of rubber compounds in an easily accessible form. Ordinarily these data are spread throughout the literature and are not indexed. The Formulary takes advantage of recently developed punched card systems and records data of rubber compounds with marginal notches. By means of these notches and regular marginal holes, it is possible with the aid of a "needle" to separate the cards having the desired data from the other cards by a simple manual operation. The cards (5 × 8 inches) contain the names and sources of the articles abstracted, with the data all plainly and carefully mimeographed. A single row of punches around the edge of each card makes the coding simple. Tensile strength, elongation, and hardness are coded, and only compounds are abstracted for which at least these three properties are recorded. Two holes tell whether or not the compound contains carbon black, and eight holes tell the kind of rubber used. The remaining holes are for special properties in which the user may be interested. The cards in the Formulary, which is now in its third year, are distributed monthly to subscribers. The Formulary is easy to use, is a thorough coverage of the literature (journals and company reports and data sheets), and fills a long-felt want. [H. L. Fisher in *Chemical and Engineering News*.]

INDUSTRIAL RESEARCH LABORATORIES OF THE UNITED STATES. Ninth Edition, 1950. Compiled by Myron J. Rand. Published by National Research Council, National Academy of Sciences, Washington, D. C. Cloth, 6½ × 10 inches, 450 pages. Price, \$5.—A measure of the growth of industrial research in the United States is found in this ninth edition of the National Research Council's directory, "Industrial Research in the United States". In gathering material for this edition between January and June, 1950 explanatory letters and information forms were sent to about 7000 companies, including the 2443 in the eighth edition. Of these latter, all but about 300 reported continued research activity; the book contains no unrevised information. Of the 4500 organizations not represented in the eighth edition, 3000 replied, and about 750 previously unreported research laboratories were found. In some cases many almost independent laboratories are grouped under a single company head, so actually the number of industrial laboratories might be considered greater than the number listed. As in previous editions, the president, research director, and assistants are listed for each company. Total professionally trained members as chemists, physicists, engineers, etc. are given, together with other technical personnel and the administrative, clerical, maintenance, etc., of the research

staff. Trade associations and research institutes are also listed, and an innovation in this edition is the indication whether the laboratory provides consulting services. The type of research done is indicated, and "research" for the purposes of this book includes industrial development work as well as fundamental and applied research, but does not apply to laboratories concerned only with production control or commercial testing. The appendix contains a listing of federal government laboratories and also a listing of university and college laboratories that provide services to industry. Included also is a geographical distribution of laboratories and a subject index to research activities. [From the *India Rubber World*.]

ROAD SURFACE PROPERTIES. (Bulletin No. 27.) Issued by the Highway Research Board, National Research Council, Washington 25, D. C. $7 \times 9\frac{1}{2}$ in., 24 pp. 45c per copy.—This bulletin contains a committee report and reproduction of a paper delivered at the 29th Annual Meeting of the Highway Research Board, held in 1949. The report is that of the Board's Committee on Anti-Skid Properties of Road Surfaces, while the paper is "Field Experiments with Powdered Rubber in Bituminous Road Construction", by T. E. Shelbourne and R. L. Sheppe, both of the Virginia Department of Highways. [From the *Rubber Age of New York*.]

STRETCHING HIGHWAY DOLLARS WITH RUBBER ROADS. By Harry K. Fisher. Natural Rubber Bureau, 1631 K St., N.W., Washington 6, D. C. 6×9 in., 36 pp.—Brought up to date by the author, rubber road consultant to the Natural Rubber Bureau; the 1951 edition of this booklet incorporates all the facts, experiences, and conclusions developed to this point with regard to the use of rubber in roads. It describes the various methods by which rubber powder is now being added to asphalt and makes full use of on-the-job photographs and statistics to cover all of the 1950 tests and review the earlier ones. Other uses for natural rubber-asphalt combinations are also suggested in the booklet. [From the *Rubber Age of New York*.]

TLARGI YEARBOOK, 1951. The Los Angeles Rubber Group, Inc., Mayfair Hotel, Los Angeles 14, Calif. Volume X. 80 pages.—Following the format of previous editions, this yearbook lists the Group's officers, directors, and committeemen; describes the work of the committees; reviews the social and technical aspects of meetings held during 1950; lists the Group's membership; gives a tabulation of Pacific Coast rubber manufacturers and suppliers; and gives the Group's bylaws. The technical section includes tabulations of elastomer-to-metal adhesives, rubber solvents, rubber reinforcing resins, and carbon blacks. [From the *India Rubber World*.]

LABORATORY DESIGN. Edited by H. S. Coleman. published by the Reinhold Publishing Corp., 330 West 42nd St., New York 18, N. Y. 9×12 in., 404 pp. \$12.00.—Written under the auspices of the Committee on Design, Construction, and Equipment of Laboratories of the National Research Council, this book contains the most complete information on laboratories ever published. It is divided into four major parts, as follows: (1) General Discussion of Materials, Facilities, Services, and Equipment; (2) Teaching Laboratories; (3) Industrial Laboratories, and (4) Concise Descriptions of Some Modern Laboratories. The latter part will prove of major interest to most users of the

book, since it is complete with plans, sections, and photographs. Among the modern laboratories analyzed in this section are those of the Bell Telephone Co., the Johns-Manville Corp., the Esso Standard Oil Co., and the B. F. Goodrich Co. Among the college laboratories discussed are those of the Illinois Institute of Technology, Reed College, Drake University, and Mellon Institute. In all, there are 42 detailed chapters by qualified experts. The book is a welcome addition to the technical literature. [From the *Rubber Age of New York*.]

PLASTIZICERS. D. N. Buttrey. Interscience Publishers, Inc., 250 Fifth Ave., New York 1, N. Y. Cloth, $5\frac{1}{2} \times 8\frac{1}{2}$ inches, 183 pages. Price, \$4.25.—This volume is essentially a working handbook on plasticizers that have either already found commercial application or appear to have future importance in the plastics industry. Information appears on some 400 plasticizers, grouped in chemical classes. For each plasticizer are given its composition, properties, advantages and disadvantages, and a bibliography of references. Plasticizer-type classifications include phthalate esters, phosphoric acid derivatives, glycerol and glycol derivatives and esters, esters of adipic and sebacic acids, fat acid esters, abietic and ricinoleic acid esters, toluenesulfonic acid derivatives, dephenyl derivatives, miscellaneous types (including camphor, anilides, urea derivatives, substituted phenols, etc.), and hydrocarbon and aromatic extenders. The final chapter presents a brief survey of theoretical aspects of plasticizers and is intended for those not already in the field. A general bibliography, list of tables, and author and subject indices are appended. The value of this work as a source of practical and convenient data on plasticizers is self-evident. [From the *India Rubber World*.]

ARTIFICIAL FIBERS. By R. W. Moncrieff. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York 16, N. Y. $5\frac{1}{2} \times 8\frac{1}{2}$ in., 314 pp. \$4.50.—This book represents a thorough coverage of the artificial, synthetic or so-called man-made fibers, including the historical and background development, the more important manufacturing processes, the chemical and physical properties of the various fibers, and, finally, specific uses of the fibers discussed. The book is divided into five sections, the first treating with the structure and properties of the fibers, the next three dealing with specific types of fibers, such as regenerated cellulosic, regenerated protein, and synthetic fibers; the last with processing methods. Among the brand-name fibers discussed are Tenasco, Durafil, Fortisan, Aralac, Vicara, Nylon, Perlon, Vinyon, Saran, Orlon, Polythene, and Plexon. Brief reference is made to rubber and some of the plastics. Suggestions for further reading are made at the end of each section. [From the *Rubber Age of New York*.]



ABRASION RESISTANCE AND ITS MEASUREMENT *

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INTRODUCTION

It is appropriate to consider first of all the definition of the term abrasion resistance, as in the past it has been used loosely throughout the rubber industry. The literal meaning of the term is the resistance to damage by scraping or rubbing. As is pointed out in a British Standards publication¹, "the abrasion resistance is commonly represented by its inverse, the abrasion loss, which, in the absence of absolute or standard methods of measurement, can be defined only as the volume of rubber abraded from a specified test-piece when subjected to abrasive wear under specified conditions." It is well known that the measurement of hardness of rubber depends on the shape and material of construction of the indenter, and therefore hardness as measured at present cannot be regarded as a specific property of rubber². In the same way the abrasion resistance of rubber depends on the "dynamic indenter", *e.g.*, both shape and material of abradant, and cannot be regarded as a specific property. Further, the result depends on the method and machine used.

Accepting the view that abrasion resistance is a complex property of materials, we find that terms such as "scratch hardness", "cutting hardness", and "abrasion hardness" have been used widely by metallurgists. These vague and ill-defined terms are used to describe particular problems, and the best that can be said is that each is associated in some way with hardness and in some way with abrasion. The confused state of definitions and test procedures in these two fields is illustrated by the fact that some workers³ have tried to measure the hardness of metals and other materials by means of abrasion or wear tests. The hardness of a material may be related to its resistance to abrasion, but no rubber technologist would be prepared to accept measurements of abrasion resistance as estimates of hardness or *vice versa*. In other words, whatever the relation between abrasion and hardness may be, it is undoubtedly not a simple one.

Throughout the years, many attempts have been made to analyze abrasion resistance into simpler components. One of the earliest was carried out by Cosler⁴, who considered the components or characteristics of abrasion to be: (1) resistance to cutting; (2) resistance to tear; (3) resilience; (4) stress-strain relations; (5) changes in any of above by (a) heat; (b) aging; (c) light; (d) conditions of stretch or distortion.

In many ways this analysis is a reasonable one which is based on common sense arguments, and hardness or modulus is included in Item 4. Another complex property which must be considered at the same time as abrasion is cracking. Undoubtedly, once small cracks occur, *e.g.*, either atmospheric

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 26, No. 3, pages 192-217, October 1950.

cracks or flex cracks, the process of abrasion may be easier for a fixed energy input and in certain cases the reverse may be true, *i.e.*, cracks or cuts can grow easier once small fissures are initiated in an abraded surface. Therefore it is suggested that another item be added to the Cosler analysis, namely:

5 (e) atmospheric cracking or flex-cracking. It can be argued that laboratory abrasion machines must be supplemented by service tests because the laboratory machine does not measure the abrasion resistance of the finished article. The same criticism can be applied to flexing machines. Laboratory flexing and abrasion machines can give a good indication of the life of an article, but the service test is the only true indication, as the abrasion and flexing take place simultaneously in practice.

Experimental proof of the importance of each of these factors is still lacking, however, and the devising of suitable experiments is not easy, and at the present stage of our knowledge may not even be possible. One method of tackling the problem is to establish what correlations, if any, exist between abrasion measurements and the simpler physical properties. The author used this method in 1941, and regression equations rating du Pont abrasion resistance with indentation hardness and tensile strength have been published⁵. Since then the same technique has been applied to road wear tests by Thornley⁶. The regression equations from these two papers for natural rubber are, respectively:

- (1) Du Pont abrasion loss = $766 - (5.347 \times \text{Shore hardness}) - (1.039 \times \text{tension strength})$
- (2) Wear index = $331.8 - (0.808 \times \text{hardness}) - (1.510 \times \text{breaking stress})$.

In both cases it is shown that the abrasion or the wear is significantly related to both the hardness and the tensile strength, and the multiple correlation coefficient is of the order of -0.9 . This means that the above expressions provide an estimate of the abrasion resistance which corresponds closely and is as valid as the measured value.

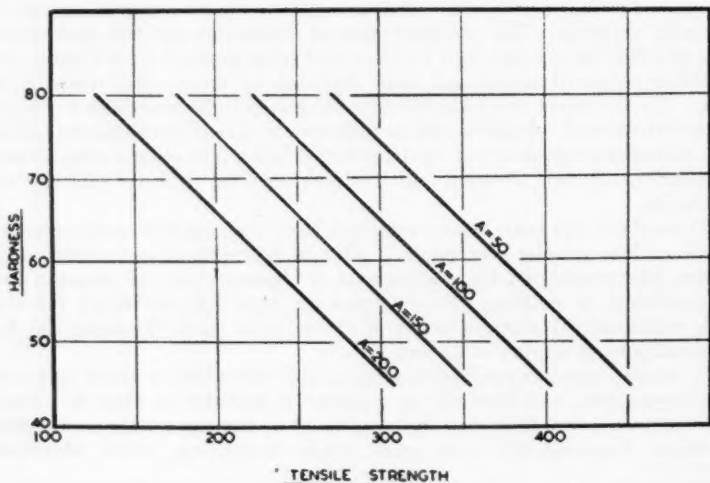


FIG. 1.

Using Equation (1), the hardness and tensile strength values corresponding to du Pont abrasion losses of 50, 100, 150, and 200 cc. have been plotted in Figure 1. It shows how in practice the technologist has a wide latitude over which he can vary the hardness and tension strength of his compound and still maintain the same abrasion loss.

The method of analyzing abrasion into simpler components by means of the regression technique does not solve the abrasion problem, but it does provide useful information. Strictly the above equations must not be used outside the range of compounds used in the determination of the data on which they are based. Nevertheless the present author takes this opportunity to quote two examples where they have been particularly useful. It is well known that with certain compounds containing waxes and fatty acids a film of these substances can clog the abrasive and hence produce a fictitiously low loss figure. A check calculation using Equation (1) has often confirmed that the abrasion resistance of such compounds was spuriously high, and has led us either to retest or in extreme cases omit the doubtful ingredients from the test mix. The second example arose in the testing of Vulkollan⁷. Material was only available for tensile and hardness tests and the abrasion loss was calculated using Equation (1). Later, when Vulkollan was tested on the du Pont machine, the experimental result agreed with the calculated result within 10 per cent.

REVIEW OF LABORATORY METHODS OF MEASURING ABRASION RESISTANCE

In the following Table 1 the majority of laboratory abrasion tests of interest to the rubber industry are listed and classified. Any tabular classification is difficult, and certain important aspects are omitted. For example, the question of whether provision is made for the cleaning of the abrasive and the removal of abraded particles has been omitted. The present author feels that this is justified, as it is now widely recognized that this factor is important and, therefore, whatever method be used, provision should be made for cleaning the abrasive by means of air jets or by brushing. This does not apply to methods in category A or method 21 in category D.

The four categories which form the basis for the classification are:

Category A — Use of loose abrasive.

Category B — Tests for fabrics, proofed fabrics, thin films.

Category C — Tests for solid rubber where the abrasion is essentially continuous.

Category D — Tests for solid rubber where the abrasion is discontinuous and the test piece is allowed to recover between the abrasion cycles.

Discussing the tests in categories A, B, C and D in turn there are a few observations worth noting.

CATEGORY A

The test can be carried out by inserting the test-piece in a container with carborundum powder and tumbling the container for various times. The abrasion resistance is estimated from the weight or volume loss. With hard plastics in solid or film form a modified method has been used; a stream of carborundum powder is directed on to the surface of the test-piece. In this case it is generally the impairment of the surface qualities of the plastic that is

TABLE 1
TYPES OF ABRASION MACHINES

Category	Name	Mechanical features	Nature of stream	Type of material tested		Comments
A	1. Falling carborundum ²²	Stream of carborundum impinging on surface	Complex	Rubbers or plastics		Simple method. Seldom used for rubber work. Used with some success to evaluate surface abrasion of plastics, <i>e.g.</i> , methyl methacrylate
	2. Sproul-Evans ⁹	Rubber rotated in cylinder containing carborundum powder	Complex	Rubbers for sandblast hose and certain types of conveyor belting.		Claimed to be the only abrasion test correlating with service wear of sand-blast hose ¹ .
	3. Martindale ²³	4 test-pieces. Abrasive normally stationary. Test-piece describes Lissajou figure during abrasion	Continuous	Textiles. Rubberized or plastic-coated fabrics. Thin polymer films. Packaging materials		The testing conditions in methods 3 and 4, <i>e.g.</i> , type of abrading, load on test-piece, can be varied. Methods of assessing the results have not been standardized, but in many cases the normal weight loss wear curve gives the required information
B	4. Wyzenbeek ¹⁴	4 test-pieces. Test-piece stationary under tension. Abrasive held on drum which oscillates by means of cam	Continuous	Textiles. Rubberized or plastic-coated fabrics. Thin polymer films. Packaging materials		
	5. Schiefer ²⁴	Test-piece and abradant both rotate. Movement designed to produce uniform abrasion over test-piece surface	Continuous	Felt. Textiles. Rubberized or plastic-coated fabrics		
	6. Du Pont Scrub ²⁵	Single test-piece, folded, held by two oscillating clamps moving in opposite directions	Continuous	Felt. Textiles. Rubberized or plastic-coated fabrics		The property measured is a combination of adhesion, flex-resistance, and abrasion

Category	Name	Mechanical features	Nature of stress	Type of material tested	Comments
C	7. Du Pont-Graselli-Williams ³⁸	Test-piece stationary, abrasive disc moves in a vertical plane. Power loss controlled by Prony brake	Continuous	General rubber compounds, e.g., tire treads, soles, heels	Machine most widely referred to in national specifications throughout the world. Results can be expressed as volume loss or loss per H.P.-hr.
	8. National Bureau of Standards ³⁹ *	Test-piece stationary, abrasive revolves on drum. Simple design	Continuous	General rubber compounds. Soles and heels	Results are expressed in terms of the number of revolutions per 0.1 inch thickness worn. Good correlation with sole and heel compounds is claimed ³⁸
	9. New Jersey Zinc Co. ³⁹	Test-piece normally stationary, abrasive is a moving circular track	Continuous	General rubber compounds	Results are expressed as volume loss. In one modification of the apparatus, the test-piece can be alternately raised and lowered from contact with the abrasive by means of cams. Claimed that original model overemphasized hardness of test-piece
	10. A. P. Conti Abrasion ⁴⁰	Test-piece bonded to metal is stationary. Abrasive fitted and moves on eccentrically mounted roller	Continuous	Tread stocks. Conveyor belting	Results expressed as volume loss. Load on test-piece can be varied. Test relatively short. End point after travel of 40 meters.
	11. DVM-Schopper abrasion ⁴⁰	Test-piece moves across the abrasive, which is rotated on drum. Once in each revolution the test-piece is lifted over clamp holding abrasive	Continuous (apart from lifting over clamp)	Tread stocks. Soling compounds. General rubber compounds	This method is widely used in Germany. The results are expressed as volume loss. As in (10) end-point after travel of 40 meters

* Schidrowitz described this type of machine as early as 1916.

Category	Name	Mechanical features	Nature of stress	Type of material tested	Comments
12.	Rotating disc ⁴⁶	Test-piece is rotated in opposite direction at a higher speed than the revolving disc holding abrasive	Continuous	General rubber compounds	Results expressed as volume loss or as loss in height or thickness. As in (10) and (11), end point after travel of 40 meters.
13.	U. S. Rubber Co. ⁴¹	Both test-piece and abrasive move. Similar to DVM (11)	Continuous	General rubber compounds	Similar in principle and method of operation to the DVM (11)
14.	B.B.S.A.T.R.A. ⁴²	Two test-pieces move backwards and forwards across abrasive cloth, which is moved slowly forward	Continuous	Leather. Rubber sole and heel compounds	Decrease in thickness of test-piece is indicated continuously. Correlation with service wear is difficult ⁴³ , and method is used mainly for development work.
D 15.	Dunlop ⁴⁴ (Lambourn)	Both test-piece and abrasive are driven. The per cent slip between test-piece and abrasive can be controlled by Eddy current brake	Discontinuous	Tire treads	Working at 16 per cent slip, good correlation with service is claimed for limited range of tire tread compounds. Useful for development work. Referred to in B.S. 903, 1950. An improved model has been referred to by Parkinson ⁴⁵
16.	Goodyear ⁴⁶ (Vogt) (Angle)	Either the test-piece or the abrasive (or both) are driven with the test-piece at an angle to abrasive	Discontinuous	Tire treads	Similar in principle to Dunlop ⁴⁷ and the Goodyear model is used quite widely in U.S.A. In America it is the next most popular method to the du Pont
17.	Akron ⁴⁸	Similar in principle to Goodyear. Employs smaller test-piece. Abrasive moves at approximately $\frac{1}{2}$ speed of Goodyear	Discontinuous	Tire treads	Similar in principle to Goodyear

Category	Name	Mechanical features	Nature of stress	Type of material tested	Comments
18.	Akron/Croydon ⁴⁸	Similar to Akron. Modified test-piece holder and provision for cleaning abrasive	Discontinuous	Tire treads	The variables associated with this method, which is included in B.S. 903-1950, have been studied in detail by the R.A.B.R.M.
19.	Kelley ⁴⁹	Both test-piece and abrasive move. Test-piece is strip clamped to periphery of wheel. Action similar to Flipper flexing machine (1)	Discontinuous	Tire treads	This method is crude, and many factors are uncontrolled.
20.	Goodrich ⁵⁰	Full details not known. Test-piece is miniature pneumatic tire	Discontinuous	Tire treads	Sufficient information on the method is not yet available. May be similar to Dunlop (15) and Goodyear (16) in essential principles
21.	Armstrong Cork ⁵⁰	Both test-piece and abrasive move. 8 test-pieces. Abrasive is in form of long roll of sand paper moving in opposite direction to test-piece	Discontinuous	Wide range of materials, including zinc and general rubber compounds	The great advantage claimed for this method is non-clogging of the abrasive as a new abrasive surface is continuously presented and each of the eight test-pieces is abraded in turn. The use of zinc as a standard for checking the abrasive is recommended. This is discussed later in the present paper.

being studied, and one method of assessment is to measure the amount of light scattered from the scratches and abrasions introduced into the surface⁸.

The Sproul-Evans⁹ is a simple method that could be set up in any laboratory where problems associated with sand blast hose, trailer cables, conveyor belts are of interest.

CATEGORY B

Abrasion tests for coated fabrics are still in the development stage, and an excellent review of this field has been provided by Dawson¹⁰. The use of the Martindale wear test with coated fabrics has been described by Buist¹¹, and a detailed statistical analysis of the various sources of error arising in this test has established the limits of error in each case, which enables comparisons of different materials to be made with some degree of confidence¹². This analysis has shown that, although errors due both to runs and to positions exist, it is possible to eliminate these by using a Latin square design. When more than four samples have to be tested, rather more complicated designs involving the use of Youden's Squares can be used¹³.

The Wyzenbeek abrasion tester¹⁴ is used in the United States, and the method is under review by Committee D11 of the A.S.T.M. From limited experience with this test, the author prefers the Martindale. The obvious difficulty with both tests, in fact all four tests in this category, is associated with assessing the end point of the test.

The Schiefer test¹⁵ has many attractive features; probably the most important is continuous measurement of the abrasion during the test by means of a condenser thickness gauge. The design of this equipment is well worthy of study.

The du Pont scrub test measures a composite property of adhesion, flexing, and abrasion. Although the test has been of use in the I.C.I. Rubber Service Laboratories for tests on coated fabrics, it is felt that the main property under test is adhesion of the coating to the fabric.

CATEGORIES C AND D

It is apparent from Table 1 that a wide variety of methods and machines have been designed. For a detailed comparison of machines 8, 13, 9, 7, 19, 15, 16, 2, the reader is referred to Cosler's paper⁴; Klamann¹⁶ has compared numbers 15, 19, 13 and 9; Depew¹⁷ has described the following machines 13, 15, 16, 7, 9, 19, 8, 1; Dawson¹⁸ has classified different types of abrasion machines and describes numbers 18 and 16; finally attention is drawn to the detailed work on the Goodyear, Akron, Akron/Croydon and du Pont machines carried out by the R.A.B.R.M. by Daynes¹⁹, Daynes and Scott²⁰, Scott²¹, Morley and Scott²², and Newton, Scott, and Willott²³.

The main distinction between categories C and D lies in the fact that in Category D the test-piece is normally circular and there is a period of relaxation between successive impacts so that the abrasion is discontinuous. In the main, the abrasion in tests in Category C is normally continuous. Although it cannot be stated as a general rule, there is a tendency for the tests in Category D to be run at faster speeds under higher energy inputs than is the case with tests in Category C. In Category D, therefore, the rate of abrasion is higher. The tests in Category D are normally used for development work by firms making tires.

CHOICE OF METHOD

With such a multitude of machines available, we are faced first of all with the problem of choosing the best method. Depew¹⁶ was of the opinion that "most machines give about the same comparative results and the question of choice of machine rests in convenience and accuracy rather than in correlation with service." All would not agree that these different machines give the same comparative results, and it has been argued that the aim and object of an abrasion test must be good correlation with service performance²⁴. The B.S. sub-committee of I.S.O. Technical Committee 45 have considered this problem²⁵ and have agreed that the use of one test machine under one set of conditions could not give satisfactory results on all types of rubber for widely different applications, *e.g.*, tire treads, soles, flooring, etc. The choice is, therefore, between the following two alternatives: (1) Selecting a number of different test machines, each operating under closely defined conditions, each machine being particularly suitable for a certain product or type of service; (2) selecting one test machine, but varying the test conditions to suit different rubbers or service conditions.

At the first meeting of I.S.O. Technical Committee 45 in London in 1948, the following five methods which appear in national specifications were discussed as a basis for international standardization: (a) du Pont—British¹, American²⁶, and French²⁷; (b) National Bureau of Standards²⁸—American; (c) Akron/Croydon¹—British; (d) Dunlop/Lambourn¹—British; (e) DIN²⁹—German. The details of these five methods are summarized in Table 2.

The essential differences between the various methods are stated clearly in Table 2. From the published reports³⁰ of the meetings of I.S.O. committee ISO/TC/45, it is clear that considerable progress has been made in reducing the number of minor but nevertheless important differences between the various specified methods. This committee recommended that a simple machine be adopted and the du Pont test was chosen as a basis for further investigation before standardization. The principle was accepted that the laboratory test should reproduce actual service conditions as nearly as possible and work should be done to establish how the correlation between the du Pont test and service could be improved. The following sections of this paper describe some of the work that was done to provide data for the U.K. delegation to I.S.O. Committee SIO/TCI45.

USE OF ZINC PLATE AS A STANDARD TEST-PIECE

It will be seen from Table 2 that most countries, and indeed most laboratories, use a standard sample, made from a known compound, *e.g.*, tire tread-soling compound, and compare the abrasion resistance of the material under test with this standard. L. A. Wood of the National Bureau of Standards reported that work in America³¹ showed that it might be better to use a metal test-piece, *e.g.*, zinc plate, to standardize and check the power of the abrasive. At first sight this is an attractive proposition, as the metal is stable and would provide a good reference standard over a reasonably long period of time.

Test-pieces of the standard dimensions were cut from zinc plate of 98.5 to 99 per cent purity.

Before giving the detailed results it should be noted that after a few minutes run the surface of the zinc was no longer smooth, but had many deep scores across the surface (see Figure 2) and it was seen that quite large pieces of zinc had been transferred to the surface of the abrasive wheel and there was a

TABLE 2

Feature	du Pont (British, American, and French)	National Bureau of Standards (American)	Akron-Croydon (British)	Dunlop (Lambourn) (British)	DIN (German) (German)
Sample movement	Nil	Nil	Rolling skew	Rolling with slip	Sl. lateral with lift
Test temp. (and humidity in case of U.S. and French)	U.S. 27.6° C (45%) Br. 20 ± 5° C Fr. 20 ± 5° C (64%)	27.6° C (45%)	20 ± 3° C	20 ± 3° C	20 ± 2° C
Rubbing speed of sample on abrasive	U.S. All identical Br. 0.81 ft. per sec. Fr. 0.247 m. per sec.	1.18 ft. per sec. = 0.36 m per sec.	Indeterminate and variable across sample	0.97 ft. per sec. = 0.296 m. per sec.	1.03 ft. per sec. = 0.314 m. per sec.
Intensity of loading (load/ sample area of contact)	U.S. All identical Br. 3.62 kg. on 8 sq. Fr. 0.44 kg. per sq. cm.	5 lb. on 1 sq. in. = 0.352 kg. per sq. cm.	Indeterminate but about 40 lb./ sq. in. = 2.8 kg. per sq. cm.	Variable, not specified, but approx. 2 kg. per sq. cm.	1 kg. on 1.6 cm. diam. = 0.5 kg. per sq. cm.
Power into sample per sq. cm. assuming $\mu = 0.5$ (μ = coefficient of friction)	5.44 kg.-cm. per sec.	6.35 kg.-cm. per sec.	Indeterminate	28-29 kg.-cm. per sec. average but intermittent	7.85 kg.-cm. per sec.
Abrasive	U.S. No. 0 emery paper Br. 4/0 emery paper or A.150 carb. wheel Fr. 80 grit carb. paper wheel	No. 20 garnet paper	36 grit carb. wheel	A. 36 carb. wheel	No. 60 paper or cloth
Method of stating results	U.S. 3 standard stocks Br. 3 standard stocks not same as U. S. Fr. absolute no. standard stock	3 U. S. standard stocks as du Pont	3 British standard stocks as for du Pont machine		1 standard stock

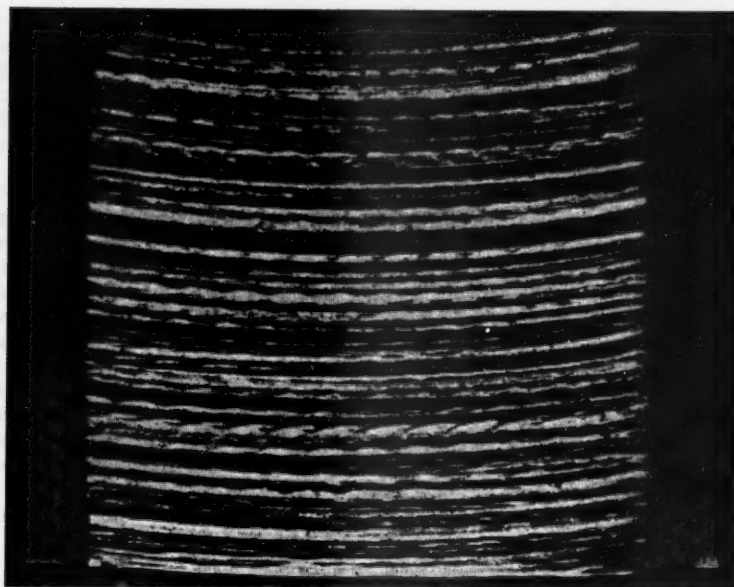


FIG. 2.

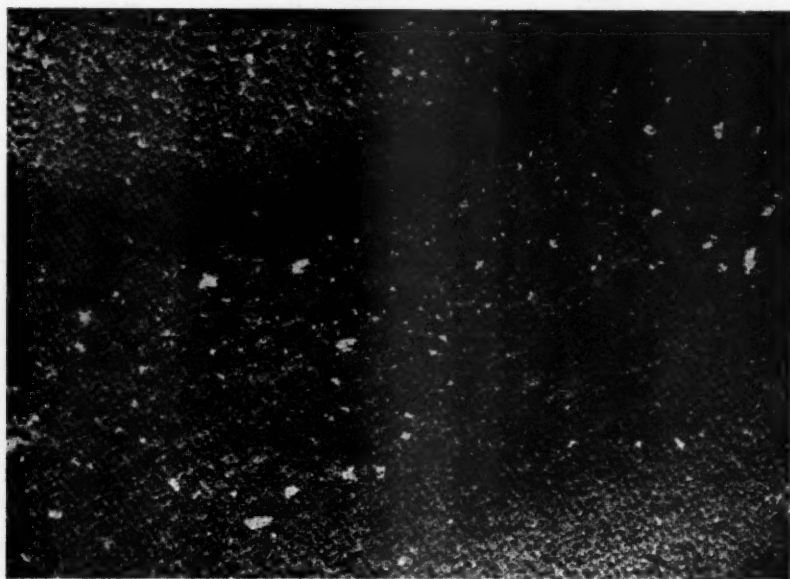


FIG. 3.

TABLE 3

	Cc. loss per H.P.-hr.	Volume loss cc. per hr.
1. Natural-rubber tread	134.3	0.842
2. Zinc plate	71.2	0.116
3. Natural-rubber tread	98.1	0.509
4. Zinc plate	35.1	0.050
5. Natural-rubber tread	84.0	0.521

tendency for the abraded zinc to fill in the interstices of the abrasive (see Figure 3). The presence of deep scores may indicate that the abrasive was uneven across its surface, but examination of the abraded rubber test-piece did not reveal any similar deep scores. It appears that as the zinc is abraded it adheres to the abrasive, smoothing the surface, and thereafter abrasion occurs only at isolated points, and the rest of the surface is merely polished by rubbing two zinc plates together. Some means must, therefore, be found of removing the abraded zinc, and it might be worth trying to increase the air pressure on the cleaning jets. In addition it was thought that better results might be obtained if a lower pressure between the test-piece and the abrasive was used. Both these modifications have been investigated, but have given little improvement in the results.

The following results (Table 3) were obtained with a load of 3.62 kg. between the zinc test-piece and the abrasive wheel.

A natural-rubber tread followed by a zinc plate were each abraded for 20 minutes, then a natural-rubber tread was abraded for 20 minutes, in an attempt

TABLE 4

	Cc. loss per H.P.-hr.	Volume loss
<i>Wheel No. X</i>		
Natural-rubber tread	125.1	0.814
Zinc plate (5-min. runs)	42.86	0.018
	28.15	0.009
	45.52	0.021
	41.78	0.020
	47.24	0.025
	48.57	0.024
	51.72	0.022
	46.66	0.017
	20.04	0.006
	39.97	0.017
Natural-rubber tread (20 min. run)	78.39	0.486
<i>Wheel No. Y</i>		
Natural-rubber tread	121.3	0.768
Zinc plate (5 min. runs)	56.35	0.021
	45.54	0.018
	35.99	0.017
	34.47	0.015
	42.06	0.022
	43.52	0.021
	44.92	0.023
	43.72	0.021
	41.55	0.019
	47.53	0.023
Natural-rubber tread (20 min. run)	93.07	0.591

to clean the abrasive, and finally the zinc plate was tested again for a further 20 minutes. As the results show, the attempt to clean the abrasive was unsuccessful, and the power of the abrasive is reduced considerably after testing the zinc for the first time. It will be noted that the abrasion loss of the natural-rubber tread is considerably reduced, and that the loss when the zinc is tested for the second time is reduced by more than 50 per cent.

There is no significant change in the abrasion loss of the natural-rubber standard (between Test 3 and Test 5). The abrasion loss of the zinc plate was measured in a series of 5-minute runs, and the results are given in Table 4. It will be seen that there is reasonable agreement between the results obtained with the two wheels, and at first sight it appears that the use of zinc (or another suitable metal) should be studied further. From visual inspection both wheels were contaminated with zinc, but there was no sign of the volume loss decreasing with increasing time.

Although the same level of volume loss is obtained with both abrasives on the zinc plate, it was necessary to check these wheels, using a natural rubber tread. The natural rubber tread was tested for 20 minutes before and after testing the zinc test-pieces. The results after testing the zinc are much lower than the initial results and show that these abrasive wheels could not be used to test rubber test-pieces after testing zinc.

TABLE 5

Wheel No.	Cc. loss per H.P.-hr.	Volume loss cc. per hr.
1	127.1	0.793
2	150.7	0.874
3	135.2	0.834
4	143.1	0.892
5	132.8	0.855
6	111.7	0.719
7	132.3	0.873
8	132.9	0.850
9	143.1	0.892

The authors³¹, who recommend this method in America state that the standard material, *e.g.*, zinc, should have an abrasion loss comparable to that of the material to be tested. The results in the present paper illustrate quite definitely that the volume loss with a rubber tread stock is 5 to 10 times greater than the volume loss obtained with zinc under the same conditions on the du Pont machine. The present author feels that the use of zinc as a standard material for checking the power of the abrasive for the du Pont machine cannot be recommended. The method may be satisfactory, however, for the Armstrong-cork machine, where the abrasive is continually renewed.

VARIABILITY OF ABRASIVE POWER OF BONDED ABRASION WHEELS

Throughout this work, bonded abrasion wheels type A.150 were used. Nine wheels were tested, using the natural-rubber tread stock R.6450 (see Appendix I), and the results were obtained for the 20 minutes' normal run. Wheels numbers 1, 3, 5, 7 and 8 were chosen for this program of work, and the other four wheels were discarded. As the results show, there is a considerable variation in the abrasive power of the individual wheels and it appears that there is much to be said for the French system²⁷ of checking the abrasive power and discarding those wheels or papers having an abrasion index outside specified

limits. The above results show that there is about 3 to 5 per cent coefficient of variation between replicates to the same specification when new and further tests on the above wheels have shown that after 3 to 4 months use another drift of 5 to 10 per cent occurs. Previous work at Croydon²¹ has shown how the variations in the power of the abrasive can affect the abrasive indices relative to a standard compound.

The details of the mixes used are given in Appendix I and it is sufficient to list the different compounds here.

1. Natural rubber	soling compound	R.5434
2. Natural rubber	heel compound	R.5438
3. GR-S	soling compound	R.5432
4. GR-S	heel compound	R.5436
5. Neoprene	soling compound	R.5433
6. Neoprene	heel compound	R.5437
7. Perbunan	soling compound	R.5431
8. Perbunan	heel compound	R.5435
9. Natural-rubber tread	45 pts. M.P.C. black	R.8331
10. Natural-rubber tread	60 pts. M.P.C. black	R.8332
11. Natural-rubber tread	45 pts. ultrafine furnace black	R.8333
12. Natural-rubber tread	60 pts. ultrafine furnace black	R.8334
13. Natural rubber-tread	46 pts. M.P.C. black	R.8759
14. Natural-rubber tread	35 pts. M.P.C. black	R.8760
	25 pts. H.M.F. black	
15. Natural-rubber tread	52 pts. H.M.F. black	R.8761
16. Natural-rubber tread	51 pts. H.M.F. black	R.8762
17. Natural-rubber tread	47 pts. M.P.C. black	R.8763
	111 pts. tread reclaim	
18. Natural rubber tread	55 pts. M.P.C. black	R.8764
19. Natural-rubber tread	47.5 pts. M.P.C. black	R.6450
20. GR-S tread	50 pts. M.P.C. black	R.6655

One of the test conditions which can be altered readily on the du Pont machine is the pressure between the test-piece and the abrasive wheel. Tests were, therefore, carried out under the following loads: 1 kg., 1.81 kg., 3.62 kg., 5.43 kg. The abrasion losses after 20 minutes in each case are given in Table 6. Reference should also be made to Figures 4 and 5, where the abrasion loss under

TABLE 6
ABRASION LOSS (CC.)

Mix	1 kg.	1.81 kg.	3.62 kg.	5.43 kg.
R.5434	0.065	0.16	0.41	0.79
R.5438	0.20	0.375	1.00	1.20
R.5432	0.05	0.15	0.33	0.65
R.5436	0.12	Samples sticky		0.825
R.5433	0.025	0.12	0.195	0.43
R.5437	0.07	0.535	1.225	1.89
R.5431	0.025	0.06	0.16	0.27
R.5435	0.02	0.04	0.125	0.21
R.8331	0.2	0.455	1.09	1.90
R.8332	0.12	0.22	0.52	0.89
R.8333	—	0.375	0.84	1.59
R.8334	0.06	0.21	0.60	0.96
R.8759	—	0.435	1.04	1.94
R.8760	—	0.325	0.94	1.65
R.8761	—	0.17	0.51	0.84
R.8762	—	0.24	0.857	1.475
R.8763	—	—	1.00	1.80
R.8764	—	—	1.41	2.225
R.6450	0.195	0.375	0.84	1.38
R.6655	0.09	0.35	0.90	1.71

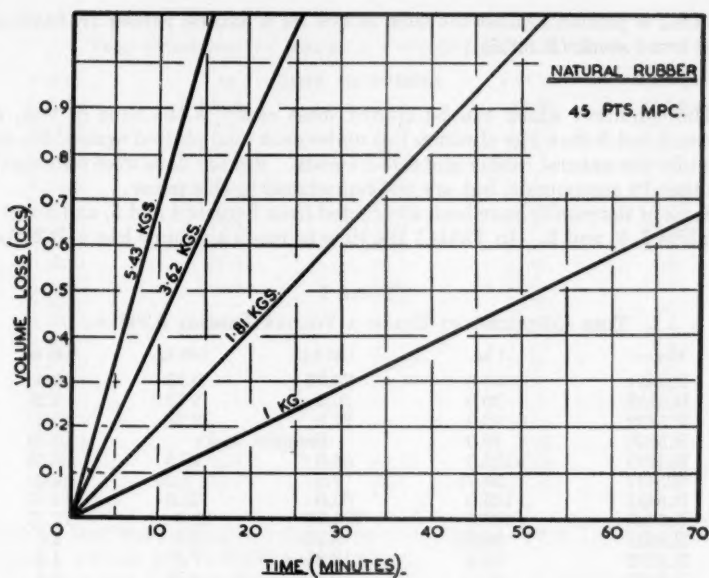


FIG. 4.

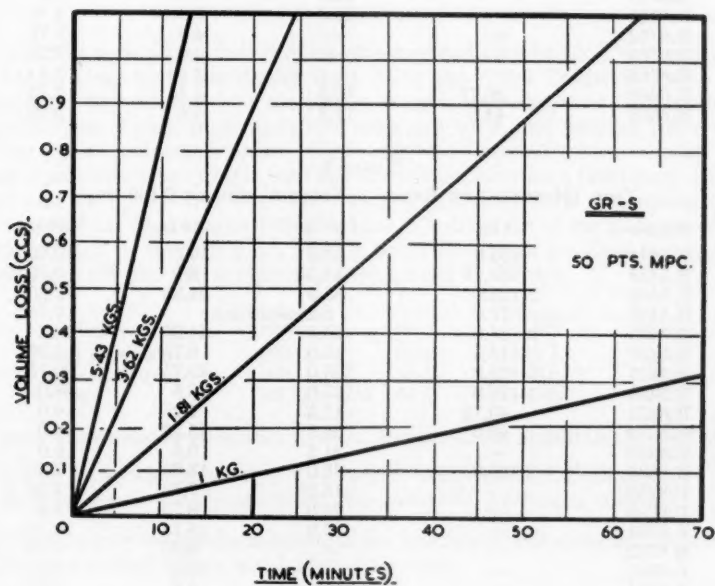


FIG. 5.

each load is plotted against the time of test for a natural rubber (R.6450) and GR-S tread stock (R.6655).

EFFECT OF TIME

The condition which can be altered most easily is the time of test, and Figures 4 and 5 show the abrasion loss under each load plotted against the time of test for the natural rubber and GR-S treads. Similar data were obtained for the other 18 compounds, but are not reproduced in this paper.

Some of the results have been abstracted from Figures 4 and 5, and are given in Tables 7, 8, and 9. In Table 7 the time to reach a volume loss of 0.200 cc.;

TABLE 7
TIME (MINUTES) TO REACH A VOLUME LOSS OF 0.200 CC.

Mix no.	1 kg.	1.81 kg.	3.62 kg.	5.43 kg.
R.5434	63.0	24.75	9.75	5.0
R.5438	20.0	10.5	3.75	3.25
R.5432	80.0	27.0	12.25	6.0
R.5436	39.0	Samples sticky		4.75
R.5433	>125.0	34.0	20.5	9.25
R.5437	58.75	7.5	3.25	2.0
R.5431	>125.0	63.0	25.0	14.75
R.5435	>125.0	101.75	29.0	19.25
R.8331	20.25	8.75	3.5	2.0
R.8332	34.0	18.25	7.5	4.5
R.8333	—	10.5	4.75	2.5
R.8334	66.25	19.0	6.75	4.0
R.8759	—	9.25	3.75	2.25
R.8760	—	12.5	4.25	2.5
R.8761	—	24.0	8.0	4.75
R.8762	—	—	4.5	2.75
R.8763	—	—	4.0	2.25
R.8764	—	—	2.75	2.04
R.6450	20.75	10.5	4.75	2.75
R.6655	44.5	11.5	4.5	2.25

TABLE 8
TIME (MINUTES) TO REACH A VOLUME LOSS OF 0.400 CC.

Mix no.	1 kg.	1.81 kg.	3.62 kg.	5.43 kg.
R.5434	125.0	50.0	19.5	10.25
R.5438	39.75	21.25	8.0	6.75
R.5432	>125.0	55.0	24.25	12.25
R.5436	77.0	Samples sticky		9.75
R.5433	>125.0	66.5	41.25	18.54
R.5437	113.5	15.0	6.75	4.25
R.5431	>125.0	123.0	49.75	29.75
R.5435	>125.0	>125.0	58.5	38.0
R.8331	40.75	17.5	7.25	4.0
R.8332	69.0	36.5	15.25	9.0
R.8333	—	21.5	9.5	5.0
R.8334	>125.0	38.0	13.25	8.25
R.8759	—	18.25	7.75	4.25
R.8760	—	24.0	8.75	5.0
R.8761	—	47.0	15.75	9.75
R.8762	—	—	0.25	5.75
R.8763	—	—	8.0	4.5
R.8764	—	—	5.5	3.75
R.6450	41.75	21.25	9.75	5.75
R.6655	87.75	23.0	9.0	4.75

TABLE 9
TIME (MINUTES) TO REACH A VOLUME LOSS OF 0.600 CC.

Mix no.	1 kg.	1.81 kg.	3.62 kg.	5.43 kg.
R.5434	>125.0	74.5	29.25	15.25
R.4538	59.5	32.0	11.75	10.0
R.5432	>125.0	82.0	36.5	18.5
R.5436	114.25	Samples sticky		14.50
R.5433	>125.0	99.5	62.0	27.75
R.5437	>125.0	22.5	10.0	6.50
R.5431	>125.0	>125.0	73.0	44.25
R.5435	>125.0	>125.0	87.5	57.0
R.8331	61.5	26.5	11.0	6.5
R.8332	113.5	55.0	23.0	13.5
R.8333	—	32.25	14.25	7.5
R.8334	>125.0	57.25	20.0	12.5
R.8759	—	27.5	11.75	6.5
R.8760	—	36.75	13.0	7.5
R.8761	—	69.25	23.5	14.5
R.8762	—	—	14.0	8.5
R.8763	—	—	12.0	6.75
R.8764	—	—	8.25	5.75
R.6450	62.5	31.75	14.25	8.50
R.6655	>125.0	34.5	13.25	7.0

in Table 8 the time to reach a volume loss of 0.400 cc.; and in Table 9, the time to reach a volume loss of 0.600 cc. are given.

To assess the value of these results obtained on the du Pont machine, it is necessary to consider the rating of the different compounds in service.

TESTS WITH SOLE AND HEEL COMPOUNDS

The first eight mixes, details of which are given in Appendix I, were supplied by I.C.I., Limited, to the British Boot, Shoe and Allied Trades Research Association. The mixes, which are purely experimental and were made without consideration of cost, were made into soles and heels, and wearing trials were carried out on postmen's boots. The methods of assessing wear of soles and heels in service are not simple, and any correlation between a laboratory assessment and the results of a wear trial depends on the methods of assessing both the results from the test and from the trial. Full details of the methods of assessment used by the B.B.S.A.T.R.A. in these wear trials are given in the published reports⁹², and the compounds were graded as follows:

Rubber	Natural rubber	GR-S	Neoprene -GN	Perbunan
Soling materials	100	68.3	41.1	16.7
Heel materials	100	40.5	54.6	43.8
Average	100%	54%	48%	30%

In order of decreasing resistance to wear, therefore, the materials are graded:

Soling materials: Natural rubber, GR-S, Neoprene-GN, Perbunan.

Heel materials: Natural rubber, Neoprene-GN, Perbunan, GR-S.

Considering now the results obtained in the laboratory test given in Tables 6 to 9, there are several points which should be noted.

- (1) From the du Pont results there is no evidence of poor abrasion with the GR-S heel mix (R.5436).

- (2) The order of the sole and heel compounds on the du Pont test is almost the complete reverse of service.
- (3) It is interesting to note that the Neoprene-GN mix (R.5433) and the Perbunan mix (R.5431) have the same abrasion loss with the 1-kg. load, but as the load is increased, so the loss with the Neoprene-GN increases much more rapidly than does the Perbunan.
- (4) Although the Neoprene heel mix (R.5437) has a lower abrasion loss than the natural rubber heel (R.5438) at 1 kg., the Neoprene-GN has the higher loss with the 5.43-kg. load.
- (5) Both the Perbunan mixes (R.5431 and R.5435) have very low abrasion loss under all conditions.

It should also be noted that the abrasion tests carried out on the B.B.S.A.T.R.A. machine give no indication even of the order in which the materials should be placed⁵³.

To obtain the same grading as was obtained from the wear trials, the test conditions on the du Pont machine would have to be altered for each material, and from the results given earlier in this paper it appears that the following conditions should be used.

- (a) With natural rubber, a small load (1 kg.) and times of test of the order of 60 minutes would be required.
- (b) With GR-S, a small load (1 kg.) and slightly longer times of test, *e.g.*, 80 minutes, would be required.
- (c) With Neoprene-GN, a time of 35 to 40 minutes with the 1.81 kg. would be required.
- (d) With Perbunan, a much higher load of 3.62 or 5.43 kg. should be used, or 70 minutes with the 1.81 kg. load.
- (e) For the GR-S heel mix, a higher load of 5.43 kg. and a time of test of 10 minutes would appear to give the desired result.

These conclusions are given, not because they solve the problem, but because they illustrate what a wide difference in testing conditions are necessary to correlate the results in the laboratory and in service with this range of mixes. It is not claimed that this method of choosing suitable conditions of tests is practicable; in fact it is emphasized that the large volume of work involved in providing the background of results from which to choose the conditions is prohibitive.

One of the aims of this work was to see whether the conditions of test could be estimated from measurements of simpler physical properties, such as hardness, as earlier work⁵⁴ had indicated that this type of approach would be useful. With these compounds, however, no solution to the problem along these lines was possible.

It must be pointed out that the case investigated where the polymer itself is being changed is probably the most difficult case to solve, and a much smaller variation in conditions might be necessary when comparing different natural rubber sole and heel mixings. Unfortunately a series of natural rubber sole and heel mixings whose service life was known was not available.

TESTS WITH TIRE TREAD COMPOUNDS

Data were available on the service life of four compounds which had been tested as part of cooperative work between Henley's Tyre & Rubber Co., R.A.B.R.M. and I.C.I., Ltd. The paper describing the results of this work

where the road wear trials were planned on a statistical basis is about to be published⁵⁵. Similar data on the wear rating of six natural rubber compounds were made available to the I.S.O./TC/45 Committee by E. F. Powell of the Dunlop Rubber Co. Du Pont abrasion tests were carried out by the present author on these ten compounds, and the effect of varying the load and the time of test was determined. Note that the lower the rating, the better is the resistance to wear.

The 10 compounds must be considered as a set of 4 and as a set of 6. The results obtained on the du Pont with a 3.62-kg. load after a run of 20 minutes for the above 10 compounds are given in Table 10. The figures in brackets

TABLE 10

Mix no.	Service wear rating	du Pont cc. per H.P.-hr.	Rating	du Pont volume loss, cc. per hr.	Rating
R.8331	100	166.4	(100)	1.125	(100)
R.8332	119.1	79.9	(48)	0.523	(46.6)
R.8333	111.6	124.7	(75)	0.787	(70)
R.8334	126	81.9	(53.5)	0.602	(53.5)
R.8759	100	154.0	(100)	1.071	(100)
R.8760	110	122.1	(79.1)	0.930	(87.0)
R.8761	125	76.4	(49.7)	0.509	(47.5)
R.8762	135	121.7	(78.9)	0.857	(79.9)
R.8763	132	147.1	(95.6)	1.014	(94.9)
R.8764	169	236.7	(154.0)	1.507	(147)

have been obtained by rating compounds R.8331 and R.8759 as 100 to simplify the comparison with service. The service wear rating is also given.

The results in Tables 6 to 9 for these compounds show that:

- (1) Under all conditions the compound containing 45 parts of ultrafine furnace (R.8333) has a lower abrasion loss than the compound containing 45 parts of MPC (R.8331). The reverse is found in service.
- (2) At all loads the compounds containing 60 parts of black (R.8332 and R.8334) have lower losses than those containing 45 parts of black (R.8331 and R.8333). Again the reverse is true in service, and the differences found from road tests, though slight, are significant.
- (3) Dealing with the set of six tread compounds, it is seen that the order is: (compound with lowest loss is given first) R.8761, R.8762, R.8760, R.8763, R.8759, R.8764. The only point where there is real agreement with service is in classifying R.8764 as the worst of the six.
- (4) There is a crossover in the natural-rubber tread (R.6450) and the GR-S tread (R.6655) as the load is increased, the GR-S being graded as superior at the low pressures.

EFFECTS OF EXTRACTION

Recent work carried out in the Rubber Laboratory of the National Research Council of Canada has indicated that it may be advantageous to extract the vulcanized rubber before testing. The authors⁵⁶ found that, in the case of GR-S, laboratory results on the du Pont did not agree with road tests. They postulate that a viscous film is formed on the surface of the abrasive and this leads to low abrasion loss⁵⁷. Extraction of the vulcanized rubber, before abrasion, with ethanol-toluene azeotrope prevented the development of this film and brought about excellent correlation with road tests. It is obvious that if

such claims are verified, this technique is of very great interest to the rubber industry.

The details of the extraction process are as follows.

"The vulcanized rubber is extracted for 96 hours in the standard Soxhlet apparatus, without paper thimble, with ethanol-toluene constant boiling mixture, made from 70 volumes of 95 per cent ethanol and 30 volumes of toluene. A mixture of ethanol and toluene is distilled, the liquid boiling at a temperature of approximately 76° C being retained. The extraction with ethanol-toluene azeotrope is followed by a 24-hour extraction with 95 per cent ethanol to remove absorbed solvent from the rubber, the ethanol being changed once during this periods. The extracted rubber is then placed in a vacuum desiccator for 24 hours at room temperature, and then allowed to stand for a further 24 hours under ordinary room conditions. Towards the end of the 96-hour period with azeotrope, it is observed that the solvent no longer becomes discolored, indicating a fairly complete extraction."

In the present work, only test-specimens of the same compounds have been extracted together in the one Soxhlet apparatus. The extraction has been carried out on the normal du Pont test-pieces, two or four samples being extracted.

The ratings obtained with the different compounds on the du Pont before and after extraction are given in Table 11 along with the service ratings.

TABLE 11

Mix no.	du Pont rating (volume loss)		Service rating
	Before extraction	After extraction	
R.8331	100	100	100
R.8332	46.6	85.6	119.1
R.8333	70	125	111.6
R.8334	53.5	108	126
R.8759	100	100	100
R.8760	90.3	93	110
R.8761	49.0	85.4	125
R.8762	83.9	123.8	135
R.8763	96.1	135.6	132
R.8764	135.4	174.0	169
R.6450	100	100	—
R.6655	107	126	—

As the above results indicate, the rating after extraction is much nearer the service rating. Although all the compounds do not fall into exactly the same order as service, it is fair to say that the extraction process has brought about a considerable improvement in the correlation between the service rating and the laboratory rating.

Comparing GR-S (R.6655) and natural rubber (R.6450), however, the GR-S is rated as being 20 to 30 per cent poorer than natural rubber after extraction, and it is well known that these figures are not verified in service. In this case the GR-S rating of 107 when unextracted is nearer the service rating. It appears, therefore, that although the extraction method is of definite interest and use with one polymer, *e.g.*, either natural rubber or GR-S, it does not enable interpolymer comparisons to be made any more exactly than in the past. This point was confirmed when work on the extraction of the eight sole and heel mixes was carried out. Here the comparison is made between different polymers, and the ratings obtained after extraction did not correlate with the

service ratings any more than did the unextracted ratings. It may be that the idea of extraction is sound but a different extraction medium may have to be found for each type of polymer.

REPRODUCIBILITY OF RESULTS

In the above experiments, the extraction was carried out in a Soxhlet apparatus according to the Canadian method⁵⁶. In other words the extraction has been timed, but time alone may not be the true governing factor. The important thing may be the number of times the extraction medium is changed.

Various tests had shown that the "within sets" reproducibility was reasonable, *i.e.*, the coefficient of variation was of the order of 8 per cent, with replicate tests-pieces extracted at the same time. On the other hand, when the extractions were repeated with test-pieces from the same mix, the reproducibility between sets was good on certain occasions, but relatively frequently some spurious results were obtained. The most likely sources of variation lie in the extraction process itself and also in the difficulty of removing the solvent entirely from the test-piece during the drying periods.

INTERPRETATION OF WEAR TEST DATA

It is not the purpose of this paper to discuss the difficulties of assessing wear test data but attention is drawn to the fact that the wear index is not necessarily constant⁵⁶ throughout the whole of a wearing trial. Before exact correlations can be established between laboratory and service tests, some mathematical method of obtaining constant indices for both tests must be found. Insufficient attention appears to have been devoted to this problem in the past.

CONCLUSIONS

A review and classification of twenty-one methods of testing abrasion resistance is a necessary preliminary to judging whether the I.S.O. decision to standardize on a simple test is justified. At the present time it is clear that a universal abrasion tester, for the wide range of applications to which rubber compounds are subjected, does not exist. Also, although all or most of the twenty-one methods can be used for compound development work in relation to special applications, *e.g.*, tire treads, conveyor belts, soles, heels, and sandblast hose, the correlation with actual wear trials must be improved before the service life can be forecast from laboratory tests. It is fair to say that the more complicated an abrasion machine becomes, the narrower becomes the range of its application on the grounds of good correlation with service. Even with the present limitations a simple test, where the test variables can be varied easily, presents the only economic solution to the problem for the small laboratory in the rubber industry.

Until the mechanism of abrasion is better understood, it therefore appears that the I.S.O. decision to adopt the du Pont method as a basis for standardization is sound. The present work relating du Pont results under various conditions of test to wear trials has shown that the extraction method is interesting and gives improved correlation with service. The method in its present form cannot be considered as satisfactory; nevertheless, it is worthy of further study by other laboratories where information on wear trials is available. Finally, it is emphasized that the methods of interpreting wear test data are often unsatisfactory and the use of statistically planned experiments should be

extended. It is useless to improve test methods in the laboratory unless corresponding care and attention are devoted to wear trials themselves.

SUMMARY

Abrasion resistance is not a specific property of rubber, but depends both on the method of measurement and the machine used. The relation between abrasion resistance and the simpler physical properties, and the use of the regression technique whereby equations relating abrasion resistance, tensile strength, and hardness have been developed, are discussed. Twenty-one existing abrasion machines are reviewed and classified in one of four categories, and, wherever possible, an indication is given of the types of compound where good correlation with service is claimed. Most of the machines have been used for compound development work, but correlation with actual wear trials must be improved before the service life can be forecast accurately. Until the mechanism of abrasion is better understood the I.S.O. decision to adopt a simple method, *e.g.*, du Pont, as a basis for standardization is sound. Work with eight sole and heel compounds and twelve tire treads shows that the order of merit obtained in the normal du Pont test is almost completely the reverse of service. With tire tread compounds, extraction of the test-pieces in ethanol-toluene-azeotrope improved the correlation with service. Further work with compounds of known service wear is required, and the extraction method in its present form does not improve the accuracy of any comparison of two compounds from different polymers, *e.g.*, natural rubber and GR-S. The use of zinc as a standard material for checking the cutting power of the abrasive has been investigated and its use is not recommended for the du Pont type of machine.

ACKNOWLEDGMENT

The author wishes to thank (Miss) J. Skerrett for carrying out the experimental work described in this paper, and G. E. Williams for his valuable help. In addition, the author is grateful to the members of the United Kingdom Subcommittee on Abrasion of I.S.O./TC/45 for their helpful comments on this work.

Compound R.8331 was an orthodox tread compound containing 45 parts of medium channel black on 100 parts of rubber. Compound R.8333 was a

APPENDIX I

	R.5431	5432	5433	5434	5435	5436	5437	5438
Perbunan	100	—	—	—	100	—	—	—
GR-S	—	100	—	—	—	100	—	—
Neoprene-GN	—	—	100	—	—	—	100	—
Smoked sheet	—	—	—	100	—	—	—	100
Zinc oxide	5	5	5	5	5	5	5	5
Magnesium oxide	—	—	4	—	—	—	4	—
Stearic acid	2	1	2.5	3	2	1	2.5	3
Lubricating oil	—	—	5	—	—	—	5	—
T.C.P.	15	3	—	—	15	—	—	—
Mineral rubber	—	5	5	5	—	5	5	5
Pine tar	5	—	—	3	3	3	—	3
P.B.N.	—	1	2	2	—	1	2	2
M.P.C. black	100	90	45	90	70	60	45	60
S.R.F. black	—	—	40	—	—	—	—	—
Sulfur	1.5	2	—	3	1.5	2	—	3
Vulcafor-F	2	2	—	—	1.75	2	—	—
M.B.T.	—	—	—	1.5	—	—	—	1.25

similar compound in which the MPC black was replaced weight for weight by an ultrafine furnace black of the type manufactured from oil enriched gas, the vulcanizing ingredients having been adjusted to suit this particular type of black. Compounds R.8332 and R.8334 contained 60 parts of MPC black and 60 parts of ultrafine furnace black on 100 parts by weight of rubber.

	R.8759	8760	8761	8762	8763	8764
Smoked sheet	100	100	100	100	100	100
Sulfur	2.5	2.5	2.5	2.5	3.3	6.5
MBT	0.8	—	—	1.15	0.85	1.7
MBTS	—	0.65	0.5	—	—	—
Stearic acid	3	2.5	2.5	2.5	3	7.5
Tackol No. 2	5	—	—	2.5	5.5	8.5
Pine tar	—	4	3.5	—	—	—
Ground mineral rubber	—	—	—	—	—	8.5
Nonox HF	0.8	1	1	0.8	0.8	2
Zinc oxide	4	5	5	5	5	10.5
W.T. reclaim	—	—	—	—	—	225
Tread reclaim	—	—	—	—	111	—
MPC black	46	25	—	—	47	55
HMF black (type 1)	—	25	52	—	—	—
HMF black (type 2)	—	—	—	51	—	—

	R.6450	R.6655
Smoked sheet	100	—
GR-S	—	100
Zinc oxide	5	5
MPC black	47.5	50
Stearic acid	3	1
Pine tar	—	3
Sulfur	3	2
MBT	0.85	—
Vulcafor-F	—	1.6

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DYNAMIC SHEAR PROPERTIES OF RUBBERLIKE POLYMERS *

I. L. HOPKINS

INTRODUCTION

Among other means for measuring the dynamic elastic modulus and viscosity, or related properties, of elastomers is the measurement of the effect of the elastomer on the resonant frequency and breadth of the resonant peak of some tuned mechanical system to which it is coupled. Rorden and Grieco¹ have described an apparatus according to this scheme, in which specimens of elastomers are coupled in shear to the prongs of tuning forks. The present paper describes this test in greater detail, presents typical data obtained with it, and discusses it analytically.

TEST APPARATUS AND MATERIALS

Apparatus.—A diagrammatic sketch of the apparatus is given in Figure 1, and the appearance of the equipment is shown in Figures 2 and 3. The vernier condenser mounted on top of the oscillator is calibrated in terms of the change in frequency, at any given frequency, as a function of vernier dial change.

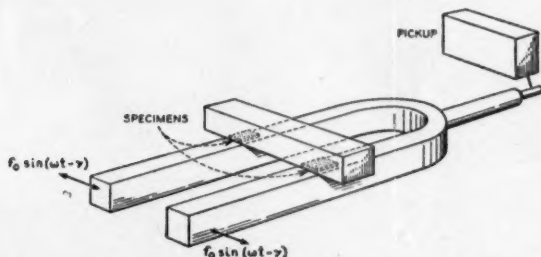


FIG. 1.—Diagram of tuning fork with driving force, specimens and pickup.

The apparatus used is given in Table 1.

The difference between the nominal and actual frequencies at the first mode are due to the loading of the pads. These were of steel $0.25 \times 0.30 \times \frac{1}{16}$ inch, and were fastened to the forks with Cycleweld. The faces of the pads were

* Reprinted from the *Transactions of the American Society of Mechanical Engineers*, Vol. 73, No. 2, pages 195-204, February 1951. An appendix containing mathematical derivations to confirm the validity of the work, and an open discussion of the paper, are omitted. This paper was presented before the Rubber and Plastics Division at the Fall Meeting of the American Society of Mechanical Engineers, Worcester, Mass., September 19-21, 1950. RUBBER CHEMISTRY AND TECHNOLOGY is indebted to the American Society of Mechanical Engineers for the electroplates, which were kindly furnished by Miss Clendinning of the editorial board.

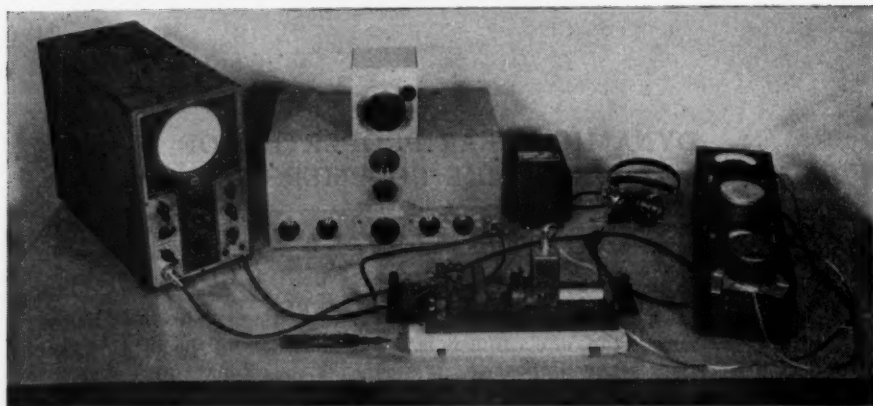


FIG. 2.—General view of apparatus.

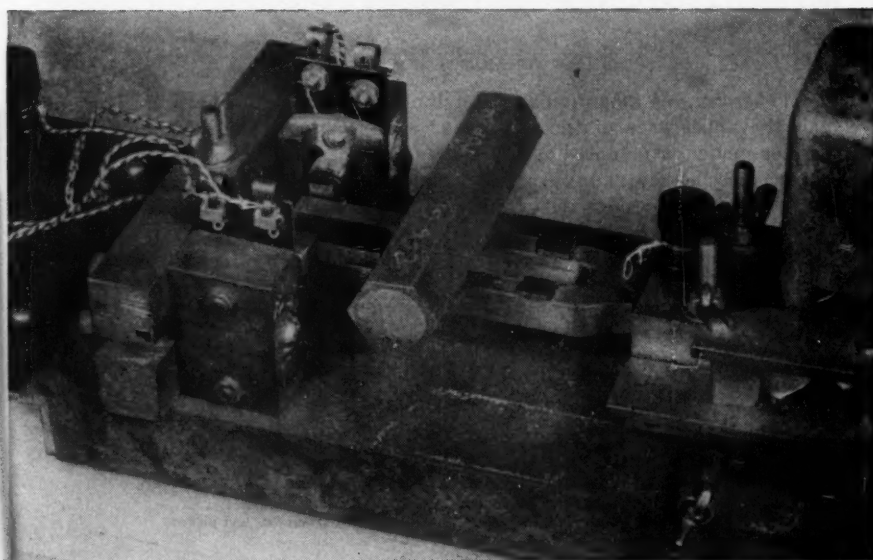


FIG. 3.—Close-up view of tuning fork with associated equipment.

then ground coplanar. The effective masses of the forks are discussed in the Appendix. The following were also used:

Pickup—Rochelle salt crystal; ammonium dihydrogen phosphate crystal for 150-deg. tests; moving coil.

Ballantine model 220 decade amplifier and model 300 a-c electronic voltmeter.

Cathode-ray oscilloscope.

TABLE 1
APPARATUS USED IN TESTS
Hewlett-Packard oscillator—201B

Tuning fork	Mode	Frequency	Position	Effective mass (grams)
100~	1	99.1	S ^a	675
			L ^b	5140
	2	1238	S	114
			L	291
250~	1	249.1	S	914
			L	30500
	2	1584	S	93
			L	963
400~	1	398.2	S	334
			L	12100
	2	2420	S	50
			L	434
900~	1	897.3	S	215
			L	4170
	2	5247	S	36
			L	438

^a Position nearer free end of prongs.

^b Position nearer base of prongs.

One set earphones, with plug to match jack in voltmeter. These were invaluable in determining the sources of disturbance causing stray pickup.

The forks were held by their shanks, with short pieces of soft-gum-rubber tubing between the shanks and the clamps. These permitted free longitudinal motion of the shank, to the end of which the pickup was applied. Some care is necessary to insure that the whole fork in the rubber mounting does not have a resonance peak near the first or second-mode peak.

Specimens.—The specimens were 0.20×0.25 inch in area and varied from 0.010 to $\frac{1}{32}$ inch thick. It was necessary that the faces be flat and parallel within close limits in order that contact over the entire face be obtained, and in cases where the specimen had unsatisfactory faces or was too thick, one or both of the faces were ground. No adhesive was used between the specimens and the fork or the bridging bar, but by careful cleaning of the metal parts and the specimen with alcohol, or by water if alcohol was inadvisable, some of the specimens were made to stick lightly to the metal in the way that newly molded rubber sometimes will.

The following materials were tested:

- 1 Butyl rubber gum M169A, with 10 min. cure at 60 lbs. per sq. in. steam.
- 2 Butyl rubber gum M169C, with 10 min. cure at 60 lbs. per sq. in. steam.
- 3 Hevea rubber gum (formula unknown).
- 4 Silicone rubber gum.
- 5 Silicone rubber—filled.
- 6 Polypropylene sebacate.
- 7 Plasticized cellulose nitrate.
- 8 Polyvinyl chloride acetate.
- 9 X6 polymerized tung oil.
- 10 X7 polymerized tung oil with dispersed polysiloxane liquid.

The compositions of these materials, in so far as we know them, are as follows:

Butyl rubber M169A	
GR-I	100
Tetramethylthiuram disulfide	1.5
Mercaptobenzothiazole	1
Phenyl- β -naphthylamine	0.5
Zinc oxide	5
Stearic acid	1
Sulfur	2.5
	<hr/> 111.5

Butyl rubber M169C—similar to M169A with 40 parts Kosmobile-77 black. Paracon AP12. Probably propyleneglycol sebacate, compounded with carbon black, and peroxide or sulfur-cured.

X6, cross-linked tung oil—a conjugated glyceride.

X7, X6 with 30 per cent by weight of polydimethyl siloxane liquid dispersed in it.

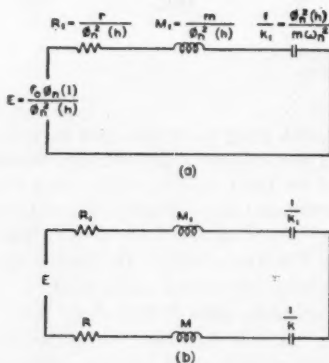


FIG. 4.—Electrical circuits analogous to (a) unloaded and (b) loaded forks.

Method of test.—The oscillator was turned on about 1 hour before starting the tests to reach temperature equilibrium. The pads and bridging bar were cleaned with alcohol, and the specimens were dipped in alcohol or water and dried on filter paper. The oscillator was adjusted for resonance of the unloaded fork with the vernier dial near the low end of the scale. Vernier dial changes for 3-decibel (db) detuning each side of resonance were read. Then the specimens were put in place with the bridging bar and similar readings made. Usually the specimens were removed, replaced, and reread for a total of five readings. The choice of the *S* or *L* position in the fork was usually forced on the operator, the loading being too great for the *S* position, or the vernier-dial changes being too slight in the *L* position.

Tests were made at room conditions (70–80° F) and at 150° F.

RESULTS OF TESTS

The results of the tests are given in Tables 2 to 4, and in Figures 5 to 14.

Discussion.—If the shear modulus g , the viscosity η , and the phase constant Q are plotted against frequency, the scatter of points about smooth curves is

TABLE 2

TEST RESULTS, MODULUS OF RIGIDITY g (DYNES PER SQ. CM.)
(All values to be multiplied by 10^6)

Material	Frequency (cycles per second)							
	100	250	400	900	1240	1580	2420	5250
At 80° F								
M169A Butyl gum	4.8	7.3	8.8	11.6	13.1	19.7	23	33
M169C filled Butyl	52	52	49	87	86	94	109	147
Hevea rubber gum	3.0	3.9	3.6	3.8	3.4	4.4	5.0	5.5
Silicone rubber gum	0.5	0.7	0.8	—	—	0.8	—	—
Filled silicone rubber	20	17	19	24	24	24	35	27
Polypropylene sebacate	10.4	10.3	11.8	12.0	17.5	13.0	15.6	18.0
Plasticized cellulose nitrate	65	66	61	106	115	134	124	254
Polyvinyl chloride acetate	12.6	17.2	21	—	38	30	—	94
X6 polymerized tung oil	—	59	60	50	—	169	142	379
X7 polymerized tung oil with dispersed polysi- loxane liquid	—	83	87	67	—	234	227	477
At 150° F								
M169A Butyl gum	3.9	3.9	4.5	5.1	6.4	5.7	6.6	8.2
M169C filled Butyl	38	22	29	33	48	45	43	83
Hevea rubber gum	3.5	3.6	3.8	4.0	4.6	4.6	5.1	5.1
Silicone rubber gum	0.7	0.9	0.9	—	—	1.1	—	—
Filled silicone rubber	11.3	9.3	12.1	12.0	15.8	15.5	20	20
Polypropylene sebacate	4.5	5.3	5.6	6.2	9.2	7.3	10.8	7.9
Plasticized cellulose nitrate	6.0	6.0	9.7	10.6	17.3	12.1	14.5	38
Polyvinyl chloride acetate	6.8	7.3	6.4	7.4	8.3	9.7	10.6	10.6
X6 polymerized tung oil	12.6	16.3	16.2	40	42	29	46	81
X7 polymerized tung oil with dispersed polysi- loxane liquid	10.5	17.5	18.2	29	45	41	51	163

manifest. Sources of error include the following:

- 1 Phase difference throughout the specimen.
- 2 Imperfect velocity response of pickup.
- 3 Uncertainty of exact size of specimen.
- 4 Imperfect adhesion to the fork or bridging bar.
- 5 Imperfect calibration of forks.
- 6 Errors in measurements of frequency changes.
- 7 Temperature variations.

Errors arising from (1) and (2) would be progressive with frequency, causing errors in the shape or location of curves, but not scatter; (3) would, in effect, cause the calculated values of η and g to be multiplied by an unknown factor, approximating unity, constant for each material since the same specimens were used for all the tests. It is suspected that (4) is the main cause of scatter. Probably (4) could be improved by actual clamping of specimens to the fork, with pads and bridging bars both above and below the fork. Errors arising from (5) would be revealed by consistent deviations from the mean curve at some one of the frequencies. No such systematic deviations were found. The error caused by (6) is calculable, and may be kept low by adjusting specimen size and thickness, and the position on the fork, within limits imposed by considerations discussed in the Appendix. Errors due to (7) are no doubt present, but the temperature variations, which were of only a few degrees, were sufficient to account for only a minor part of the total scatter.

TABLE 3
 VISCOSITY, η (POISES)

Material	Frequency (cycles per second)							
	100	250	400	900	1240	1580	2420	5250
At 80° F								
M169A Butyl gum	8000	3700	3500	2600	1550	2010	1840	1380
M169C filled Butyl	34000	13100	10400	8300	4900	5500	4400	3000
Hevea rubber gum	350	240	177	116	55	68	60	43
Silicone rubber gum	300	126	106	—	—	53	—	—
Filled silicone rubber	4100	2300	1370	720	480	420	410	180
Polypropylene sebacate	5700	2600	1790	780	740	540	380	300
Plasticized cellulose nitrate	78000	28000	15200	10200	8700	7300	5500	5600
Polyvinyl chloride acetate	23000	6300	5500	—	3500	2400	—	3500
X6 polymerized tung oil	—	38000	23000	7600	—	11700	7500	8100
X7 polymerized tung oil with dispersed polysi- loxane liquid	—	50000	32000	11000	—	10100	9700	9100
At 150° F								
M169A Butyl gum	1320	590	810	420	400	370	360	220
M169C filled Butyl	11400	3300	2900	2400	1960	1590	1060	1340
Hevea rubber gum	730	340	190	84	57	55	41	24
Silicone rubber gum	270	160	78	—	—	43	—	—
Filled silicone rubber	3100	1150	1050	420	330	290	220	100
Polypropylene sebacate	2600	1300	820	450	420	350	300	220
Plasticized cellulose nitrate	6400	2700	2200	2600	1920	1110	840	1130
Polyvinyl chloride acetate	2500	910	610	280	330	350	270	190
X6 polymerized tung oil	17300	8400	4400	3400	4000	3400	3300	2100
X7 polymerized tung oil with dispersed polysi- loxane liquid	23000	10300	5900	4000	5300	4600	3500	3800

 TABLE 4
 MECHANICAL PHASE CONSTANT, Q

Material	Frequency, cycles per second							
	100	250	400	900	1240	1580	2420	5250
At 80° F								
M169A Butyl gum	1.0	1.3	1.0	0.8	1.1	1.0	0.8	0.7
M169C filled Butyl	2.5	2.5	1.9	1.9	2.3	1.7	1.6	1.5
Hevea rubber gum	13.6	10.4	8.2	5.8	7.9	6.5	5.5	3.9
Silicone rubber gum	2.7	3.5	3.0	—	—	1.5	—	—
Filled silicone rubber	7.8	4.7	5.5	5.9	6.4	5.8	5.6	4.5
Polypropylene sebacate	2.9	2.5	2.6	2.7	3.0	2.4	2.7	1.8
Plasticized cellulose nitrate	1.3	1.5	1.6	1.8	1.7	1.9	1.4	1.4
Polyvinyl chloride acetate	0.9	1.7	1.5	—	1.4	1.3	1.3	0.8
X6 polymerized tung oil	—	1.0	1.0	1.2	—	1.5	1.5	1.4
X7 polymerized tung oil with dispersed polysi- loxane liquid	—	1.1	1.1	1.1	—	2.3	1.5	1.6
At 150° F								
M169A Butyl gum	4.7	4.2	2.2	2.2	2.1	1.6	1.2	1.1
M169C filled Butyl	5.3	4.2	4.0	2.4	2.6	2.8	2.7	1.9
Hevea rubber gum	7.6	6.8	7.8	8.4	7.1	8.4	8.2	6.5
Silicone rubber gum	4.1	3.6	4.6	—	—	2.6	—	—
Filled silicone rubber	6.4	5.1	4.6	5.0	5.9	5.4	6.0	6.1
Polypropylene sebacate	2.8	2.6	2.7	2.4	2.8	2.1	2.4	1.1
Plasticized cellulose nitrate	1.5	1.4	1.8	0.7	1.2	1.1	1.1	1.0
Polyvinyl chloride acetate	4.3	5.1	4.2	4.7	3.2	2.8	2.6	1.7
X6 polymerized tung oil	1.2	1.2	1.5	2.1	1.6	0.9	0.9	1.2
X7 polymerized tung oil with dispersed polysi- loxane liquid	0.7	1.1	1.1	1.3	1.4	0.9	1.0	1.3

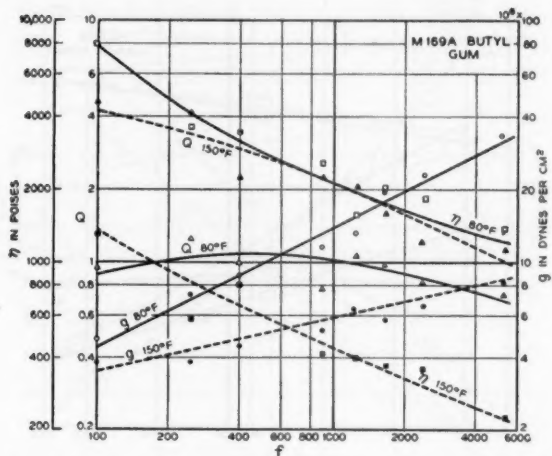


FIG. 5.—Dynamic shear properties of Butyl rubber gum M169A, as a function of frequency.

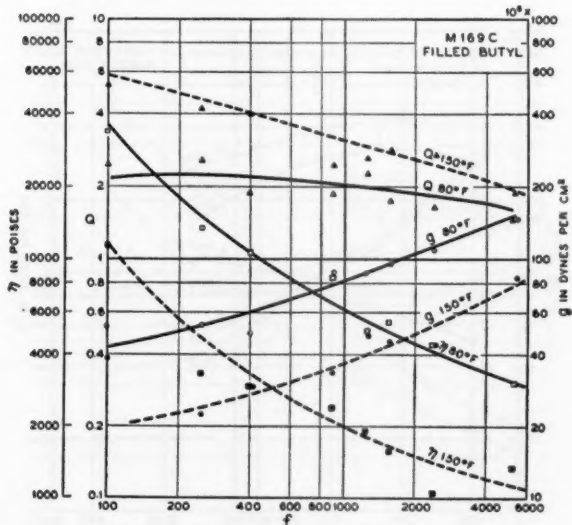


FIG. 6.—Dynamic shear properties of loaded Butyl rubber M169C as a function of frequency.

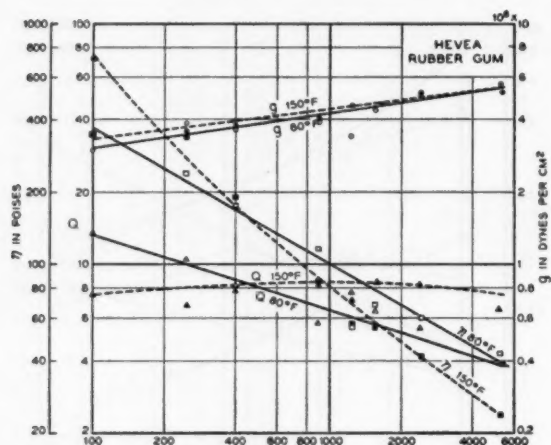


FIG. 7.—Dynamic shear properties of Hevea rubber gum as a function of frequency.

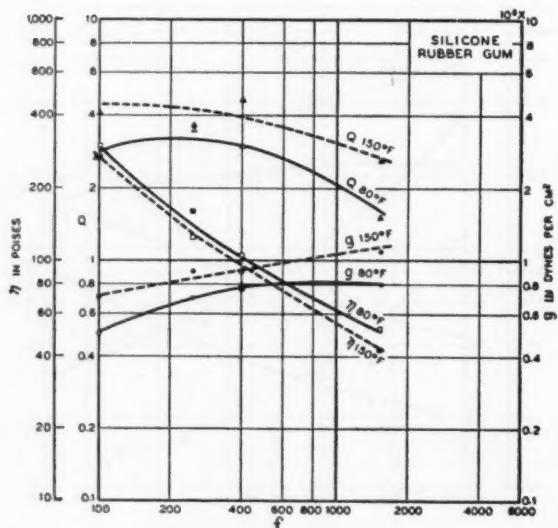


FIG. 8.—Dynamic shear properties of silicone rubber gum as a function of frequency.

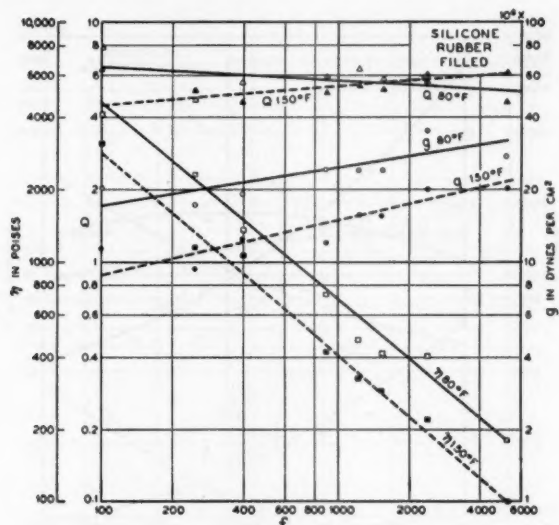


FIG. 9.—Dynamic shear properties of loaded silicone rubber as a function of frequency.

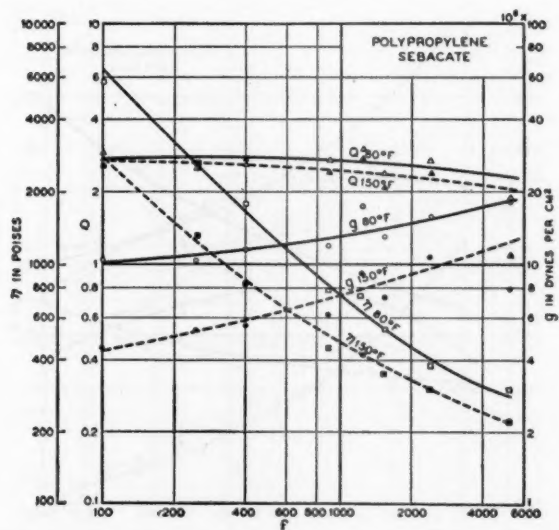


FIG. 10.—Dynamic shear properties of polypropylene sebacate as a function of frequency.

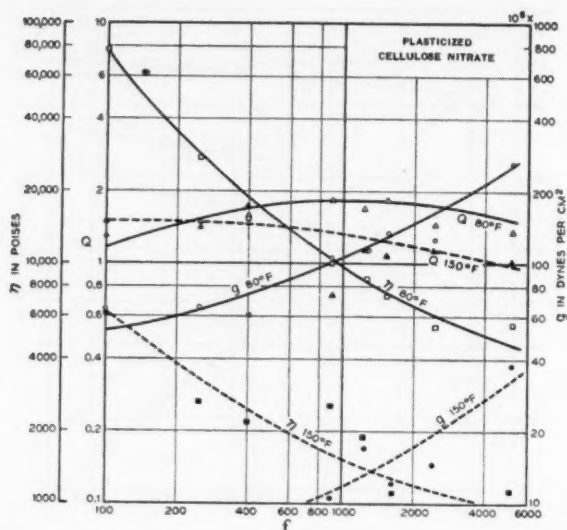


FIG. 11.—Dynamic shear properties of plasticized cellulose nitrate as a function of frequency.

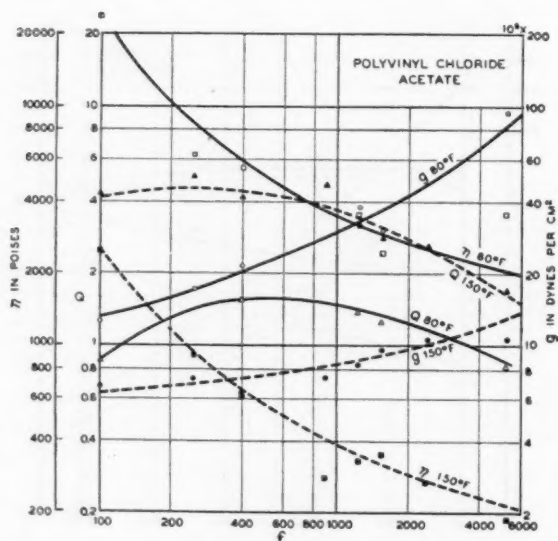


FIG. 12.—Dynamic shear properties of polyvinyl chloride acetate as a function of frequency.

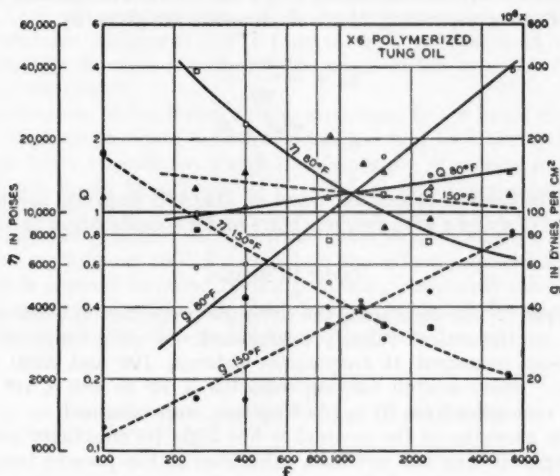


Fig. 13.—Dynamic shear properties of X6 polymerized tung oil as a function of frequency.

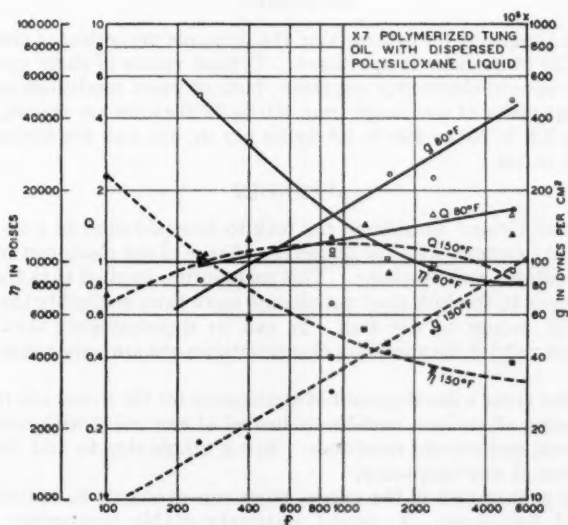


Fig. 14.—Dynamic shear properties of X7 polymerized tung oil with dispersed polysiloxane liquid as a function of frequency.

The shear modulus and viscosity were computed on the assumption of a series electrical circuit, corresponding to a Voigt model with parallel mechanical elements. The corresponding Maxwell elements are given by:

$$\eta_m = \frac{\eta^2 \omega^2 + g^2}{\eta \omega^2}$$
$$g_m = \frac{\eta^2 \omega^2 + g^2}{g}$$

The distributions of relaxation times of Maxwell elements associated with the variations of η and g with frequency are under consideration at present.

CONCLUSIONS

A technique (2) for measuring the dynamic properties of elastomers is discussed, and its theoretical validity established. A wide range of elastomer types has been measured at frequencies between 100 and 5250 cycles per second (cps). Shear moduli varying from 0.5×10^6 to 480×10^6 dynes per sq. cm., and viscosities from 20 to 75,000 poises, were obtained.

While the precision of the method is not high, its simplicity and possible frequency range (which has not been exhausted in the present tests), and its yielding of data in terms of shear properties, recommend it for exploratory measurements. The advantage of the extended frequency range is manifest in avoiding the short-range conclusion that g and $\omega\eta$ are constants.

SUMMARY

A simple apparatus for determining the dynamic properties of elastomers in shear at audio frequencies is appraised. Typical values of shear modulus and viscosity for several elastomers are given, both at room conditions and at 150° F. The frequencies of test range from 100 to 5250 cycles per second, the shear moduli from 0.5×10^6 to 480×10^6 dynes per sq. cm. and the viscosities from 20 to 75,000 poises.

APPENDIX

Rorden and Grieco¹ considered the fork to be equivalent to a simple mass-spring-viscosity system, with the added impedance of the elastomer represented by a series stiffness and viscosity. This assumption implied that the coupling of the elastomer to the fork does not change more than negligibly the forms assumed by the prongs of the fork. It can be demonstrated that these assumptions are valid if the specimen characteristics are properly related to those of the forks.

Young² has given a development of expressions for the forms and frequencies in free vibration of uniform cantilevers loaded at any point with combinations of spring, mass, and viscous resistance. It is a simple step to add the effect of a driving force at any frequency.

Since the preparation of the paper, some improvements have been made in experimental technique. A second relatively stable comparison oscillator makes it possible to measure small frequency changes in the driving oscillator accurately by timing the pattern on the oscilloscope screen. This use of only small frequency changes is a considerable theoretical advantage and results in data which are more accurate than previously obtained.

The manifestation of higher viscosity in silicone gum at 150° F than at 80° F at 250 cycles is probably due to scatter, as this material was so soft as to be at the lower limit of measureability. It is interesting to observe, however, that the shear modulus is higher at 150° F than at 80° F, as is required by the kinetic theory, although the ratio is somewhat in excess of the value 339/300, or 1.13, required by the theory.

Reconsideration of the Hevea rubber gum leads to the belief that there may have been slippage between the rubber and the fork or bridging bar, particularly at the lower frequencies where the amplitude of motion is the greatest. This condition would be aggravated by the fact that the specimens were not only thinner than any of the other and, therefore, subject to greater strains at a given displacement, but also had no surface tackiness. There is some indication of increased modulus at 150° F but not to the extent required by the kinetic theory. It is planned to retest Hevea gum using somewhat thicker specimens of a known compound. The new tests should provide clarification of all of the doubtful features of the data on Hevea given above.

REFERNECES

- ¹ Rorden, H. C., and Grieco, A., Memorandum, Bell Telephone Laboratories, Inc.
- ² Young, *Trans. Soc. Mech. Engrs.* 70, A-65 (1948).

RHEOMETRIC TESTS AND EXTRUSION *

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During a study of extruders, the need was felt to know more completely than was permitted with the use of existing plastometers the rheological properties of extruded materials.

A cylindrical rheometer of the Couette type suitable for rubber and rubber compounds was, therefore, designed to obtain the rheometric curve $D - \tau$, where D = rate of shear in seconds⁻¹ and τ = shear stress in kg. per sq. cm.

The purpose of this study was strictly practical, and therefore precise equipment was not employed.

Mooney¹ and Hamm² have already used cylindrical rheometers for tests on rubber. Mooney applied a pressure to the material from the outside by means of two retaining rings. This pressure is selected with reference to τ , and ranges from 0 to 5.6 kg. per sq. cm. According to Mooney, the maximum τ values are 2 kg. per sq. cm. and shear rates, 100 seconds⁻¹.

Hamm used a rheometer derived from that of Mooney, but without movable rings. He therefore relied on the pressure generated when the instrument closed, which pressure was not determined. The τ values reached did not exceed 1 kg. per sq. cm. and the highest rates of shear were about 1 second⁻¹; these are not high enough to be of practical interest. Hamm states that the instrument does not allow for the use of shearing stresses of the same magnitude as those that occur during the technical procedures to which rubber and rubber mixtures are exposed in manufacturing practice, for example, the forcing process. This is the chief limitation of his accurate work. In the rheometers of both Mooney and Hamm, rotor and stator have longitudinal grooves to prevent the material from slipping on the walls.

A noncylindrical rheometer, but with a constant rate of shear, has been used by Piper and Scott³; this is a shearing cone plastometer derived from Mooney's shearing disk plastometer. The pressure used is as high as 30 to 60 kg. per sq. cm., and tests are made for imposed rates of shear from 0.01 to 10 seconds⁻¹. A continuous-shear rheometer developed by Pollett and Cross⁴, has recently appeared.

The widest rheometric curve is that reported by Mooney, relating to low milled rubber tested at 100° C (pale crepe). Piper and Scott plot two typical curves for natural rubber and GR-S. A comparison between the rheometric curves obtained by different investigators has been made by Scott and Whorlow⁵. The data available from the technical literature, therefore, are scarce for elevated rates of shear, as Hamm's most ample experimental material concerns only very low rates of shear.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 479-487, February 1951. This paper was presented at the International Meeting of the Division of Rubber Chemistry of the American Chemical Society, Cleveland, Ohio, October 11-13, 1950.

RHEOMETRIC TESTS

Description of Rheometer.—The cylindrical rheometer, shown in Figure 1, is derived from the viscometer of Searle⁶.

Two coaxial and independent cylinders, *A* and *B*, having diameters of 3.2 cm. and lengths of 3 and 6 cm., respectively, are mounted one in each end of a cylindrical chamber with a diameter of 3.4 cm. bored in the housing of the device. The cylinders extend into two shafts of smaller diameter, on which the chamber is closed so as to leave a free annular bore; these shafts turn in the thrust and radial ball-bearings placed in the housing. Each of the two shafts is rigidly connected with a grooved pulley, *C*, and recording drum, *D*. Two pendulums, *E*, fastened to the frame, record the rotational speed of the cylinders on the drums.

Warm water, supplied from a separate apparatus, circulates in the chamber walls, which are honeycombed with bores. At the center of the chamber between the heads of the two cylinders, a small feeding extruder projects; its axis

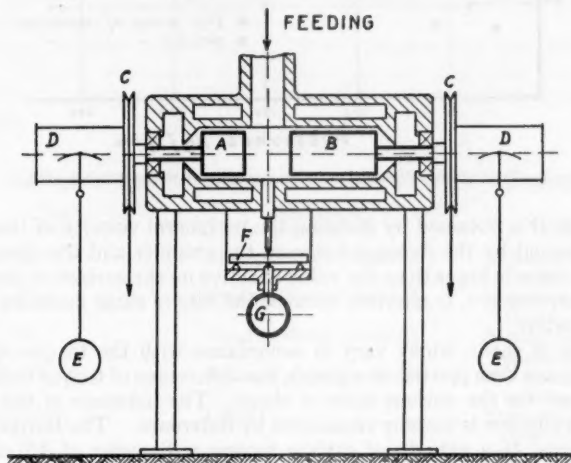


FIG. 1.—Schematic drawing of cylindrical rheometer.

is orthogonal to the axis of the cylindrical chamber. Inside the chamber a plunger having a cross section of 1 sq. cm. is also fitted suitably between the cylinder heads. This plunger transmits the thrust given by internal pressure to a flat spring, *F*, fixed at both ends; the deflection is read on a dial gage, *G*. The pressures shown depend on the type of material, and in the test reported here were between 25 and 250 kg. per sq. cm. The pressures are plotted against a rheometric constant, *c*, in Figure 2.

The normal procedure used was as follows:

The instrument was filled by feeding the extruder until the material issued from the annular openings smoothly and continuously. Weights, increasing by steps, were then applied by means of a small flexible wire cord to the grooved pulley, and the angular displacements were recorded on drums (Figure 3). Tests were made with the two cylinders simultaneously.

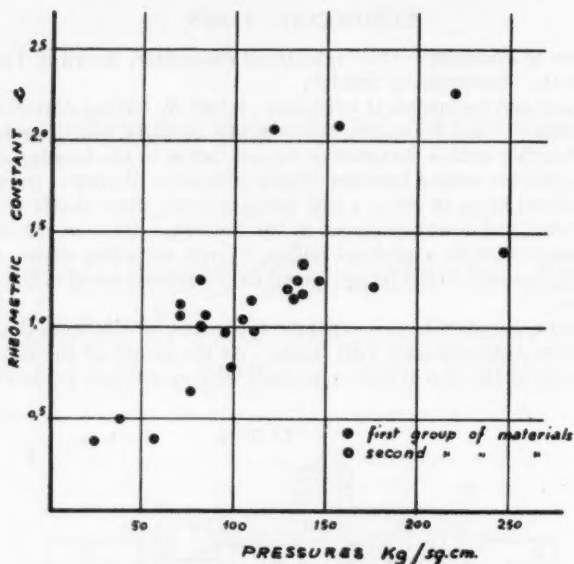


FIG. 2.—Pressures in cylindrical chamber according to rheometric constant, c .

Shear rate D is obtained by dividing the peripheral velocity of the cylinder in cm. per second by the distance between the cylinder and the chamber (0.1 cm.). This value is lower than the value effective on the surface of the cylinder to which shear stress, τ , is referred, because the rate of shear increases with the increase of radius.

The rates of shear, which vary in accordance with the torque applied to the cylinders, are then plotted on a graph, the differences of torque being graphically obtained for the various rates of shear. The influence of the terminal parts of the cylinders is thereby eliminated by difference. The torque deduced may be referred to a cylindrical surface having a diameter of 3.2 cm. and a length of 3 cm. (surface = 30 sq. cm.). Shear stress, τ , in kg. per sq. cm., is readily calculated from the difference in torque.

This procedure supposes a perfect identity between the heads and shafts of the two cylinders, whether this identity be geometrical or in relation to the material undergoing test. It is clear, for instance, that the pressure distribution is not symmetric, there being in fact a greater flow of material from the annular outlet of the shorter cylinder. The axial motion of the material due to continuous feeding therefore differs from one cylinder to the other. It must also be remembered that the effective rate of shear at each point depends on the

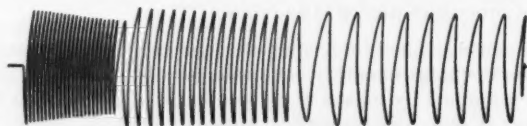


FIG. 3.—Recorded graph.

speed resulting from the composition of tangential speed, due to rotation, with the axial speed, due to the feeding. The axial speed is, however, very small and is only evident at low rotation speed. Rates of shear lower than 1 second^{-1} were determined by stopping the feeding extruder after the instrument has been completely filled. For higher rates of shear the instrument was fed continuously, and it was proved that the difference in the speed of the cylinder, whether the extruder is at rest or working, is negligible.

Another negative element of the instrument is the additional processing of the material by the feeding extruder. When the material is measured it is no longer in the same condition as it was originally.

Rheometric Determinations.—Tests were carried out at two different times on two distinct groups of materials, which were afterwards used for tests in the extruder.

Simple compounds, excluding vulcanizing elements, were used in each case to avoid scorching. The composition and processing of both groups of materials are shown in Tables I and II, where "normal" processing indicates the minimum required for the satisfactory incorporation of the ingredients. All determinations were made at 80°C .

A complete graph of test for bath 2, SD-60p (Figure 4), is reported by way of example. The two curves, $M - D$, relating to two cylinders, are plotted in semilogarithmic coordinates. The curve, $\log D - \log \tau$ is plotted at the right of the graph.

TABLE I
COMPOSITION AND PROCESSING OF FIRST GROUP OF MATERIALS

Batch no.	Batch mark	Composition of batch	Processing
1	SD-10p	Smoked sheet (washed)	10 passes between closed rolls
2	SD-60p	Smoked sheet (washed)	60 passes between closed rolls
3	SD-60'	Smoked sheet (washed)	60 minutes with mill opening of 2 mm.
4	SD-120'	Smoked sheet (washed)	120 minutes with mill opening of 2 mm.
5	GR-S-10p	GR-S	10 passes between closed rolls
6	GR-I-10p	GR-I	10 passes between closed rolls
7	SD-10-OP-10p	Smoked sheet (washed), 100; paraffin oil, 10	10 passes between closed rolls
8	SD-SOLB-60p	Smoked sheet (washed), 100; lampblack, 80	60 passes between closed rolls
9	SD-SOCC-40p	Smoked sheet (washed), 100; whiting, 80	40 passes between closed rolls
10	SD-20CC-40F	Smoked sheet (washed), 100; whiting, 20; factice, 40	Normal
11	SD-20CC-40F-60p	Smoked sheet (washed), 100; whiting, 20; factice, 40	Normal + 60 passes between closed rolls
12	SD-40F	Smoked sheet (washed), 100; factice, 40	Normal
13	GR-S-70LB	GR-S, 100; lampblack 70	Normal
14	GR-S-70LB-60p	GR-S, 100; lampblack, 70	Normal + 60 passes between closed rolls
15	GR-I-70LB	GR-I, 100; lampblack, 70	Normal

TABLE II
COMPOSITION AND PROCESSING OF SECOND GROUP OF MATERIALS

Batch no.	Batch mark	Composition of batch	Processing
1'	SD-50CC	Smoked sheet (washed), 100; whiting, 50	Normal
2'	SD-80LB	Smoked sheet (washed), 100; lampblack, 80	Normal
3'	SD-40F	Smoked sheet (washed), 100; factice, 40	Normal
4'	SD-20CC	Smoked sheet (washed), 100; whiting, 20	Normal
5'	SD-F-CC-60p	Smoked sheet (washed), 100; factice, 40; whiting, 20	60 passes between closed rolls
6'	GR-S-10p	GR-S	10 passes between closed rolls
7'	SD-40LB-10-OP	Smoked sheet (washed), 100; lampblack, 40; paraffin oil, 10	Normal
8'	GRI-20CC	GR-I, 100; whiting, 20	Normal
9'	GR-S-25EPC	GR-S, 100; easy processing channel black, 25	Normal
10'	SD-25EPC	Smoked sheet (washed), 100; easy processing channel black, 25	Normal

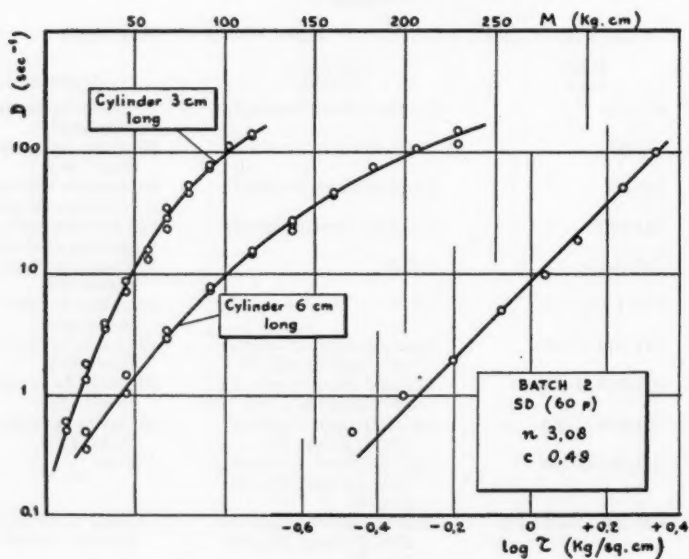


FIG. 4.—Complete test graph for one material.

The rheometric curves of all materials tested are brought together in double-logarithmic coordinates in Figures 5 and 6 for the first group of materials and Figures 7 and 8 for the second group.

The experimental points in double-logarithmic coordinates are distributed, for each material, approximately along a straight line. Some materials stray

from this course, and the straight line interpretation in these instances is somewhat arbitrary (Figure 6, batch 14 and Figure 8, batch 8').

Some observations were also made on the relative positions of the various materials. It must be pointed out, however, that the purpose of the work was

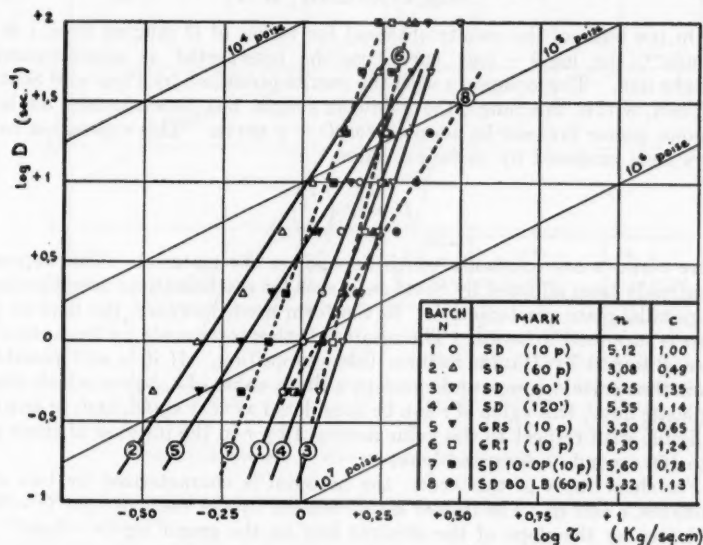


FIG. 5.—Rheometric curves—first group of materials.

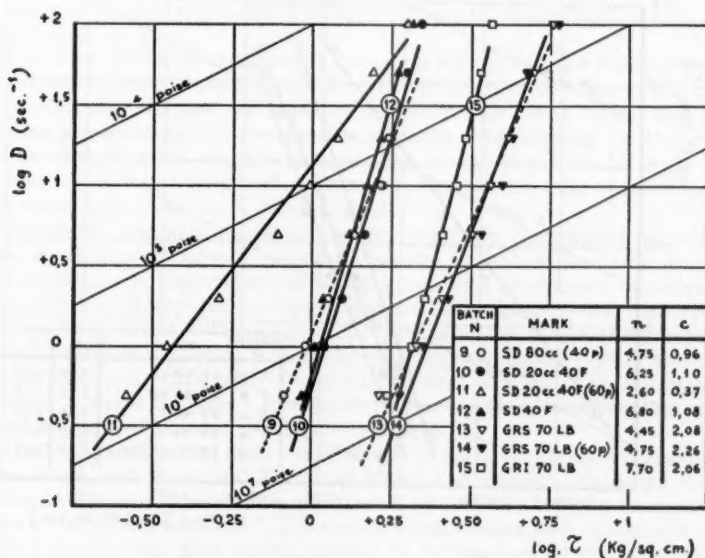


FIG. 6.—Rheometric curves—first group of materials.

to use materials with clearly distinctive rheometric characteristics but not to study the effect of the composition and processing rheologically. Consequently, the tests were not made under conditions of strict comparison.

RELATIONSHIP, $D-\tau$

On the basis of the results obtained for values of D ranging from 1 to 100 seconds⁻¹, the $\log D - \log \tau$ curve can be interpreted as approximately a straight line. This compares with the results published by Piper and Scott³.

Then, within this range, the following simple, but dimensionally nonhomogeneous, power law can be adopted for $D - \tau$ curve. This expression has already been proposed by various authors.

$$D = - \left(\frac{\tau}{c} \right)^n \quad (1)$$

where c and n are constants which depend on the material. This expression has already been adopted by Scott as a basis for mathematical investigation on the parallel-plate plastometer⁷. In the form used, however, the load at yield stress is supposed to be nil. The results of other tests made by the author and those obtained by Hamm confirm this supposition. If it is still possible to admit that certain compounds present a finite value of τ , below which there is no plastic flow⁸, this value of τ can be considered as very small, and, in any case, negligible with respect to the value assumed by τ in the interval of shear rates (1 to 100 second⁻¹) discussed here.

For shear rates of this order, the material is characterized by two single constants, c and n . The former is represented by the value of τ for $D = 1$ and the latter by the slope of the straight line on the graph $\log D - \log \tau$. The

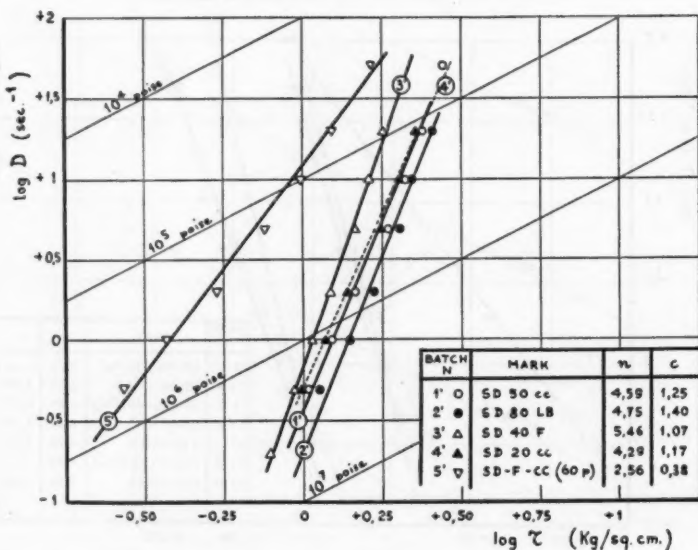


FIG. 7.—Rheometric curves—second group of materials.

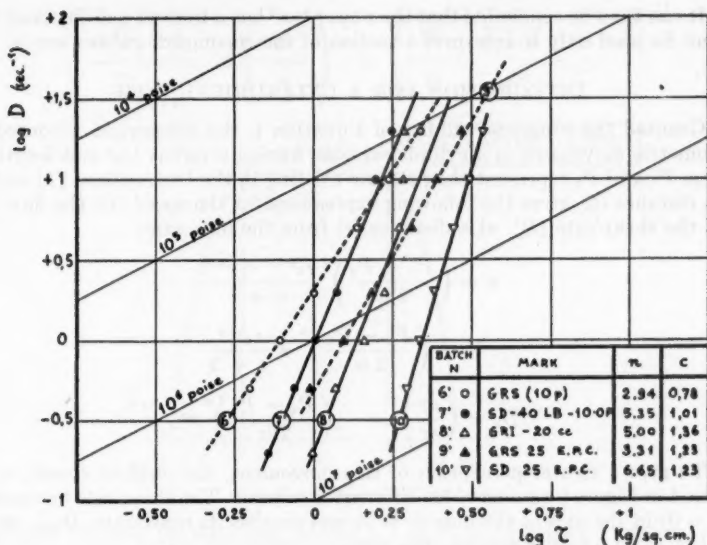


FIG. 8.—Rheometric curves—second group of materials.

values of c and n calculated for the various materials tested are reported in Figures 5, 6, 7, and 8.

Considering the course of the rheometric curve in a limited interval, the question arises as to whether extrapolation is admissible. This is because of the many difficulties encountered in its experimental determination in a wide range of shear rates.

With very low shear rates, small forces are active, and the frictions generated by the devices become preponderant. With elevated shear rates, there are considerable temperature increases in the sample being tested and high pressures are necessary to prevent the material from slipping on the walls. Here, in relation to the arguments mentioned, a comparison can be made with the work of Scott and Whorlow⁵. Moreover, the measurement of short spaces of time and high speed, is, in itself, difficult.

Philippoff⁹, operating on diluted rubber solutions, has plotted rheometric curves which tend to have a constant viscosity at both ends—lower limit η_0 , upper limit η_∞ . If this course can be explained by a mechanism of molecular orientation, we can suppose that something analogous happens also with rubber and with its solutions. The intermediate course of the $D - \tau$ curve between the two limits η_0 and η_∞ could be considered as the exponential type, with a non-constant exponent. Marzetti¹⁰ found an exponent of about 2 for low rates of extrusion, whereas for higher speeds, and therefore for higher shear rates, he indicated a deviation towards higher exponents.

Mooney himself traced some curves ($\log D - \log \tau$), which show a convexity to the τ -axis, and Scott and Whorlow⁵ found that rubber masticated for 60 minutes at the lowest attainable shear rates at 100° C., behaves in the same way as a Newtonian material. The author's experiments also, covering a wide range of shear rates, give curves, plotted in double-logarithmic coordinates, which are convex to the τ -axis.

It can then be concluded that the power law² has a limited validity and that it can be used only to interpret a section of the rheometric rubber curve.

INTEGRATION FOR A CYLINDRICAL HOLE

Granted the complete validity of Equation 1, the integration accorded the rheometric movement in a cylindrical hole, having a radius (r_0) and length (l), where P_1 and P_2 represent the pressure existing in the two sections (1) and (2) at a distance (l), gives the following expressions for the speed (v), the flow (V), and the shear rate (D), at a distance (r) from the hole axis:

$$v = \left(\frac{P_1 - P_2}{2lc} \right)^n \frac{r_0^{n+1} - r^{n+1}}{n+1} \quad (2)$$

$$V = \left(\frac{P_1 - P_2}{2lc} \right)^n \pi \frac{r_0^{n+3}}{n+3} \quad (3)$$

$$D_r = \left(\frac{dv}{dr} \right)_r = - \left(\frac{P_1 - P_2}{2lc} \right)^n r^n \quad (4)$$

To give a clearer perception of this movement, the outflow speeds, v , are plotted in Figure 9 against r , for different n values. The shear rate becomes nil ($D = 0$) in the axis of the hole ($r = 0$) and reaches its maximum, D_{\max} , on the wall ($r = r_0$) where it assumes the value:

$$D_{\max} = \left(\frac{dv}{dr} \right)_{r_0} = -v_m \frac{n+3}{r_0} \quad (5)$$

V_m is equal to $V/\pi r_0^2$ or average outflow speed.

As the shear rate assumes all values from 0 to D_{\max} , the whole rheometric curve governs the movement of the material in the same interval.

The graph showing the speed distribution, if integrated, can also represent the total flows. If this graph is cut with a straight line perpendicular to the

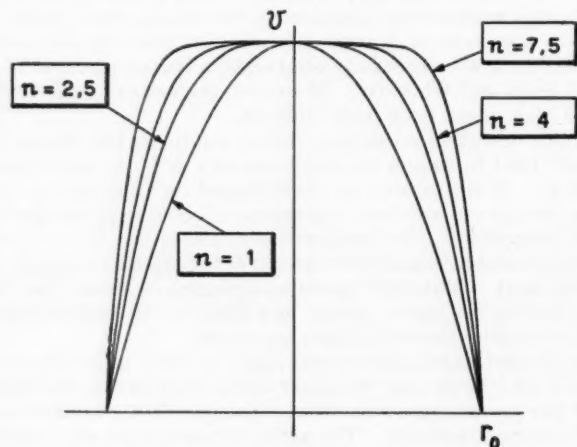


FIG. 9.—Speed distribution along diameter of cylindrical hole for various values of exponent, n .

$$\frac{D_r}{D_{\max}} = \left(\frac{r}{r_0} \right)^n = \left(\frac{W}{V} \right)^{\frac{n}{n+3}}$$

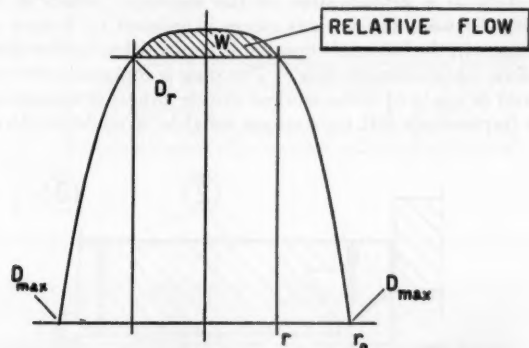


Fig. 10.—Total and relative flow.

axis hole (Figure 10), the area is divided into two portions. The flow corresponding to the shaded area can be called the *relative flow*. With K indicating the ratio between the relative flow and the total flow, V , the ratio between the shear rate D_r (at the limits of the relative flow) and the maximum shear rate on

the wall D_{\max} is given by the values $K^{\frac{n}{n+3}}$ as follows:

n	K			
	0.001	0.01	0.05	0.1
2	0.063	0.16	0.20	0.4
4	0.018	0.07	0.18	0.27
6	0.01	0.046	0.13	0.21
8	0.0067	0.035	0.11	0.19

The integration given by Equation 3 can, without excessive severity, be considered as approximate according to the value of K , as long as Equation 1 is verified experimentally from the maximum to 0.1 or 0.01 of the maximum shear rate. Moreover, as the rheometric curve is only slightly curved in double-logarithmic coordinates, it is possible to extend this concept to the whole rheometric curve as long as the proper interval is chosen for each test and the values of c and n are calculated for it. It is necessary to know n for the calculation of the highest shear rate; one must therefore proceed by trial and error, assuming an initial n value.

TESTS ON EXTRUDER

Description of Apparatus.—A normal 2-inch extruder provided with a variable-speed drive and water heating was used. Materials were fed by hand in strips of suitable size preheated to the working temperature of the extruder. The materials of the first group were used in extrusion tests with a three-orifice die, those of the second group with a die having a single orifice.

The three-orifice die, shown in Figure 11, was provided with interchangeable mouthpieces of various diameters. The pieces composing the die are shown in Figures 12 and 13. The rubber flows from left to right. The disk, 1, is in

direct touch with the terminal part of the extrusion chamber, almost in contact with the screw, and carries the material on to the pressure-measuring plunger (visible in Figure 13) and through three conical orifices at 120° C passing through 2 to the mouthpieces. These are held in place by disk 3. Screw 4 has a locking effect in a prolongation of the extruder, which is likewise water-heated. Grip between the various pieces is ensured by copper gaskets.

The pressure in the internal chamber is transmitted by the plunger terminating in a ball on an aluminum disk. The disk is replaced after each measuring operation and is made of lathe-worked drawn annealed aluminum. A calibration of the impressions left by various weights is made on disks of the same

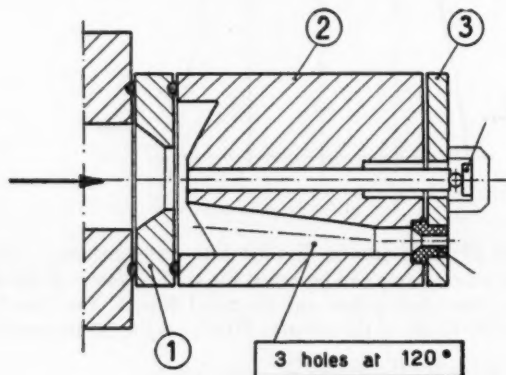


FIG. 11.—Schematic drawing of three-orifice die used for first group of materials.

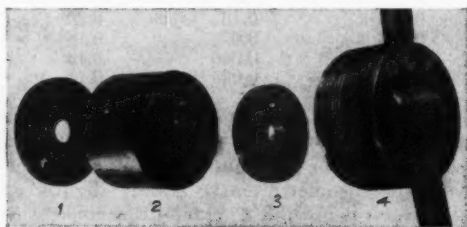


FIG. 12.—Three-orifice die. Rubber flows from left to right.

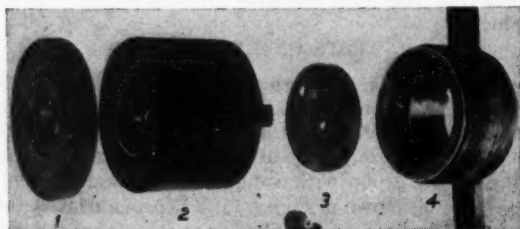


FIG. 13.—Three-orifice die. Rubber flows from left to right.

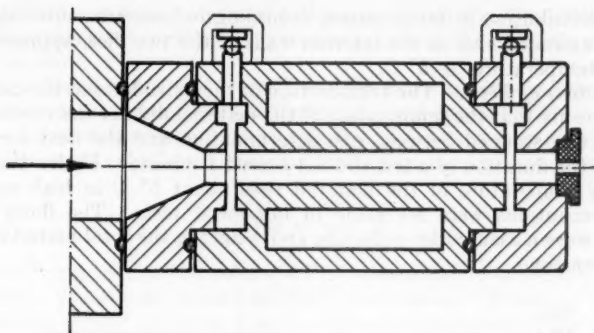


FIG. 14.—Schematic drawing of single-orifice die used for second group of materials.

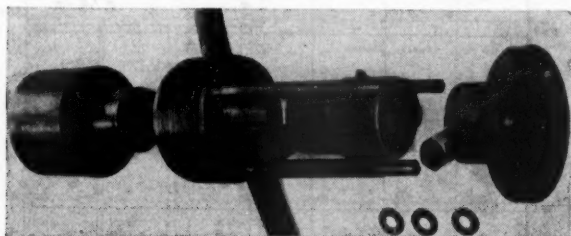


FIG. 15.—Single-orifice die.

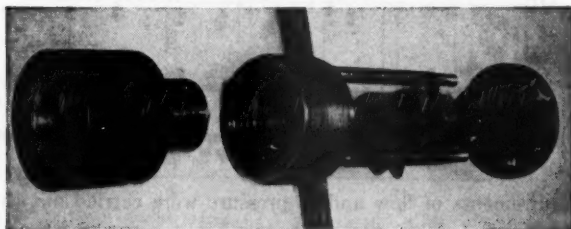


FIG. 16.—Single-orifice die.

material as described above. Pressure is then obtained on the basis of the diameter of the impression measured with a low power microscope.

For the second group of materials, a die with a single cylindrical orifice and with pressure-measuring devices in two intermediate sections was constructed. In fact, it was found desirable to deviate from the experimental conditions under which, as testified by Mooney¹¹, the preorifice work is a considerable part of the total energy required for the extrusion. At the end of the orifice a throttle device was fitted to keep the pressure along the duct at a high level, thus preventing the material from slipping on the walls.

This new die is shown in Figures 14, 15, and 16. The die is given a partial bearing in the water-heated prolongation of the extruder. The piece included between the two pressure-measuring sections is directly water heated.

The distribution of temperature, according to measurements made on the material extruded and on the internal walls of the two dies, approximates the working temperature, $\pm 5^\circ \text{C}$.

Conditions of Tests.—The temperature of the extruder and the dies was 80°C . To ensure that the temperature of the material did not rise excessively, the extruder was stopped between one determination and the next for about 10 minutes; the duration of a test did not exceed 1 minute. Under these conditions the temperature of the material rises about 5°C in high speed tests. These precautions were set aside in low-speed tests. The flows from the extruder were measured by collecting and weighing the total material extruded in a known time.

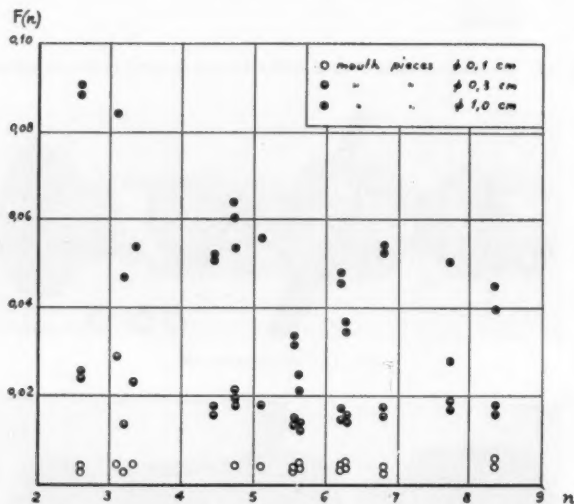


Fig. 17.—Relation between values of $F(n)$ and exponent, n , for various diameters of mouthpieces. First group of materials.

All measurements of flow and of pressure were carried out three or more times.

Results of Tests.—For exposition of the results, Equation 3 may be stated as follows:

$$\frac{V_n}{P_1 - P_2} c = \frac{1}{2l} \sqrt{\frac{\pi r_0^{n+3}}{n+3}} = F[(r_0, l), n] = F(n) \quad (6)$$

The first term is calculable from test data (V and $P_1 - P_2$) if the constants n and c of the material are known.

The second term depends on geometric dimensions and n . For a given hole it is dependent on n only. This second term also can be calculated; it is even possible to calculate from it a priori the whole course of the expression $F(n)$ concomitant with n .

With a complex die, such as that with three holes having conical and cylindrical segments, the second term is a good deal more complex but always depends only on the dimensions and the exponent, n . The difficulty of as-

certaining the dimensions exactly and the uncertainty deriving from the last cylindrical segment, where slipping probably occurs on the walls, do not permit exact calculations.

Materials Tested with Three-Orifice Die.—From the average values in kg. per sq. cm. of the relative pressure in the internal chamber and of flow V in cc. per minute for different diameters of mouthpieces and for various screw speeds, the values of $F(n)$ were calculated according to the first term of Equation 6:

$$F(n) = \frac{1}{P} V^n c \quad (6a)$$

Figures 17 and 18 give the values of $F(n)$ dependent on n , for the different, mouthpieces. There is no ordered distribution of results. However, the values are distributed around different lines for different diameters of the discharge hole.

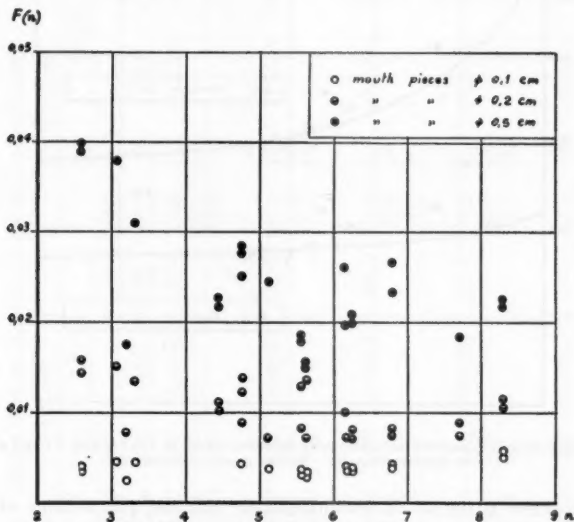


FIG. 18.—Relation between values of $F(n)$ and exponent, n , for various diameters of mouth pieces. First group of materials.

Bearing in mind that the experiments are performed on materials rheometrically very different (n from 2.6 to 8.3 and c from 0.37 to 2.26) and that tests on the extruder are carried out with flows ranging from 1 to 250 ml. per minute and with pressures from 20 to above 400 kg. per sq. cm., and considering the imperfections of the devices employed and the influence of external factors such as temperature, aging of the material, and secondary shearing effects, the agreement between the data of extrusion and the rheometric constants seems to be satisfactory. Furthermore, the highest shear rates, in many tests, are beyond the limits for which the values of n and c can be considered as correct.

Materials Tested with Single-Orifice Die.—After this first result it was desirable to control the actual agreement of values of the first term of Equation 6, calculated on the data of the extruder and on the rheometric parameters of the material, with those of the second term, calculated on the basis of the geometric

dimensions of the device and the value of n . In other words, an effort was made to determine the validity of Equation 6. It was necessary to extrude through a hole of easily measurable dimensions and to ensure that slipping on the walls did not occur. The single-orifice die fulfils these characteristics (Figure 14). The two cross-sections, where pressure is measured, are 10 cm. from each other. Measurements were made with different extruder speeds (revolutions of the screw were approximately 1, 6, 12, 20 per minute) and hole diameters of 0.7 and 1 cm.

In Tables III and IV flows in cc. per minute and pressure differences between the two cross-sections in kg. per sq. cm. are recorded with the average values for each test. Both flows and differences in pressure vary to a remarkable degree from material to material—for instance, with the 0.7-cm. mouth-

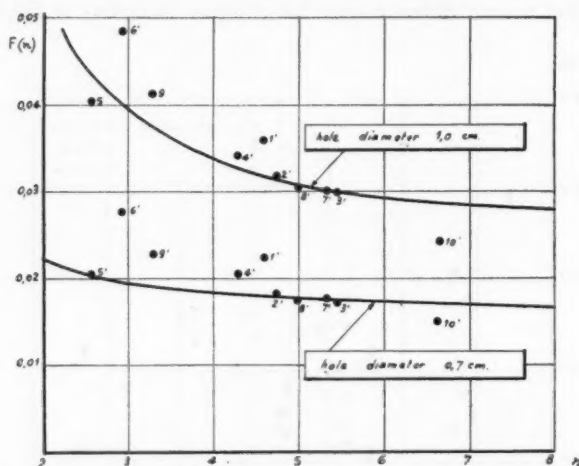


FIG. 19.—Analytical and experimental relationship between values of $F(n)$ (Table V) and exponent, n , for single-orifice die. Second group of materials.

piece, if the screw turns at 20 revolutions per minute, the volume of extruded material in cc. per minute is 19.9 for batch 10' and 51.4 for batch 2'; the pressures are 82.3 kg. per sq. cm. for batch 5' and 165.6 kg. per sq. cm. for batch 2'.

In low-speed tests, because of the small flows, the comprehensive weight of material extruded in successive tests was considered; for this reason a single value only is given in the tables (the highest shear rates on the wall are given in parentheses).

From the average values of flow and from the difference of pressure combined with the rheometric constants, c and n , of various materials, the first term of Equation 6 was calculated, and the values are given in Table V. For each hole diameter the average value of the results obtained with different speed for each material was calculated.

In Figure 19, the values of $F(n)$ dependent on n , and calculated from the second term of Equation 6, are plotted with an unbroken line:

$$F(n) = \frac{1}{2l} \sqrt{\frac{60\pi\tau_0^{n+3}}{n+3}} \quad (6b)$$

TABLE III
FLOW AND PRESSURE DIFFERENCES AND AVERAGE VALUES FOR DIE WITH SINGLE 0.7-CM. DIAMETER HOLE
(Rates of shear on wall are given in parentheses)

Batch no.	1 R.P.M.					6 R.P.M.					12 R.P.M.					20 R.P.M.				
	Flow (V) (cc./ 4 min.)		Pres- sure (ΔP) (kg./ sq. cm.)		Average	Flow (V) (cc./ min.)		Pres- sure (ΔP) (kg./ sq. cm.)		Average	Flow (V) (cc./ min.)		Pres- sure (ΔP) (kg./ sq. cm.)		Average	Flow (V) (cc./ min.)		Pres- sure (ΔP) (kg./ sq. cm.)		Average
1	11.5	61	66	72	74	2.9(2.5)	68.2	15.7	103	15.3(14)	93.5	30.0	105	29.3(28)	117.3	45.2	153	44.6(42)	149.6	
								14.3	95			28.9	123			44.1	143			
								15.9	82			29.0	123			44.6	153			
2	11.0	78	75	79	71	2.7(2.6)	75.9	17.0	141	15.8(15)	137.0	31.4	151	31.5(30)	165.3	54.3	166	51.4(50)	165.6	
								16.7	138			31.8	182			50.9	159			
								14.0	131			31.3	163			49.2	172			
3	11.4	80	76	75	76	2.9(3.1)	77.1	14.7	94	14.6(15)	100.1	22.9	107	25.2(27)	110.3	39.6	122	39.8(42)	123.8	
								14.5	94			26.0	109			40.5	128			
								14.6	111			26.6	115			39.4	124			
4	10.7	58	64	77	58	2.7(2.4)	64.5	16.3	118	16.2(15)	113.6	28.2	136	27.8(35)	132.6	37.8	131	39.4(37)	132.5	
								15.9	115			28.3	123			39.2	133			
								16.4	107			27.1	136			41.1	133			
5	10.0	23	23	22	..	2.5(1.3)	23.2	11.2	52	11.7(8.1)	52.7	22.8	66	24.4(17)	67.7	42.2	80	44.5(31)	82.3	
								11.7	51			25.2	64			45.5	84			
								12.1	54			25.4	73			45.7	83			

TABLE III—Continued

Batch no.	1 R.P.M.					6 R.P.M.					12 R.P.M.					20 R.P.M.				
	Flow (cc./4 min.)		Pre- sure (ΔP) (kg./sq. cm.)		Average	Flow (V) (cc./min.)		Pre- sure (ΔP) (kg./sq. cm.)		Average	Flow (V) (cc./min.)		Pre- sure (ΔP) (kg./sq. cm.)		Average	Flow (V) (cc./min.)		Pre- sure (ΔP) (kg./sq. cm.)		Average
					V (cc./min.)					ΔP (kg./sq. cm.)					V (cc./min.)					ΔP (kg./sq. cm.)
6'	12.0	45	3.0(2.5)	41.6	...	29.5	87	86.0	48.0	111	49.7(38)	107.0	51.6	126	50.0(52)	115.8	24.2	147	41.2(33)	149.0
						28.0	89	86.0	52.0	111	49.0	98	50.8	119	47.7	111	25.1	137	41.9	152
						15.5	36	...	27.0	82	28.2(23)	86.0	29.5	87	28.2(23)	86.0	25.1	141	40.0	152
						15.0	42	...	27.0	82	27.0	82	27.0	82	27.0	82	25.1	141	40.0	152
7'	11.7	61	2.9(3.0)	64.1	96.5	31.3	106	106.3	51.6	126	50.0(52)	115.8	50.8	119	47.7	111	25.1	137	41.9	152
						16.5	94	96.5	51.6	126	50.0(52)	115.8	50.8	119	47.7	111	25.1	137	41.9	152
						16.4	96	96.5	51.6	126	50.0(52)	115.8	50.8	119	47.7	111	25.1	137	41.9	152
						63	63	96.5	51.6	126	50.0(52)	115.8	50.8	119	47.7	111	25.1	137	41.9	152
8'	10.7	93	2.7(2.7)	93.4	137.8	17.9	131	138.2	24.2	147	24.8(25)	142.0	17.9	131	17.5(17)	138.2	24.2	147	41.2(33)	149.0
						11.7	149	138.2	24.2	147	24.8(25)	142.0	17.9	131	17.5(17)	138.2	24.2	147	41.2(33)	149.0
						11.9	132	138.2	24.2	147	24.8(25)	142.0	17.9	131	17.5(17)	138.2	24.2	147	41.2(33)	149.0
						87	87	138.2	24.2	147	24.8(25)	142.0	17.9	131	17.5(17)	138.2	24.2	147	41.2(33)	149.0
9'	9.1	73	2.3(1.8)	77.9	117.2	25.4	148	146.6	41.9	142	41.2(33)	149.0	25.4	148	25.4(21)	146.6	41.9	142	41.2(33)	149.0
						13.6	113	146.6	41.9	142	41.2(33)	149.0	25.4	148	25.4(21)	146.6	41.9	142	41.2(33)	149.0
						14.5	128	146.6	41.9	142	41.2(33)	149.0	25.4	148	25.4(21)	146.6	41.9	142	41.2(33)	149.0
						79	79	146.6	41.9	142	41.2(33)	149.0	25.4	148	25.4(21)	146.6	41.9	142	41.2(33)	149.0
10'	8.7	108	2.2(2.6)	102.9	131.8	14.6	148	140.3	18.4	147	19.9(24)	148.3	14.6	148	17.5(21)	140.3	18.4	147	19.9(24)	148.3
						11.1	131	140.3	18.4	147	19.9(24)	148.3	14.6	148	17.5(21)	140.3	18.4	147	19.9(24)	148.3
						11.1	131	140.3	18.4	147	19.9(24)	148.3	14.6	148	17.5(21)	140.3	18.4	147	19.9(24)	148.3
						11.6	133	140.3	18.4	147	19.9(24)	148.3	14.6	148	17.5(21)	140.3	18.4	147	19.9(24)	148.3
						95	95	140.3	18.4	147	19.9(24)	148.3	14.6	148	17.5(21)	140.3	18.4	147	19.9(24)	148.3

TABLE IV
FLOW AND PRESSURE DIFFERENCES AND AVERAGE VALUES FOR DIE WITH SINGLE 1-CM. DIAMETER HOLE
(Rates of shear on wall are given in parentheses)

Batch no.	1 R.P.M.						6 R.P.M.						12 R.P.M.						20 R.P.M.					
	Press- sure			Average			Press- sure			Average			Press- sure			Average			Press- sure			Average		
	Flow (V) (cc./ 4 min.)	ΔP (kg./ sq. cm.)	V (cc./ min.)	ΔP (kg./ sq. cm.)	V (cc./ min.)	ΔP (kg./ sq. cm.)	Flow (V) (cc./ min.)	ΔP (kg./ sq. cm.)	V (cc./ min.)	ΔP (kg./ sq. cm.)	Flow (V) (cc./ min.)	ΔP (kg./ sq. cm.)	V (cc./ min.)	ΔP (kg./ sq. cm.)	Flow (V) (cc./ min.)	ΔP (kg./ sq. cm.)	V (cc./ min.)	ΔP (kg./ sq. cm.)	Flow (V) (cc./ min.)	ΔP (kg./ sq. cm.)	V (cc./ min.)	ΔP (kg./ sq. cm.)		
1'	17.0	46	4.3(1.4)	41.5	22.6	76	23.4	69	23.5	65	42.9	76	42.8(14)	80.5	67.2	80	66.7(21)	82.0	64.8	81	68.0	85		
2'	8.5	38	2.1(0.7)	41.6	21.2	94	21.3	94	20.4	94	28.6	92	38.4(13)	97.3	60.7	120	62.2(21)	114.3	63.3	114	62.7	109		
3'	17.6	45	4.4(1.6)	48.4	19.7	65	19.3	64	19.8	64	34.4	66	35.0(12)	66.0	52.6	73	52.5(19)	70.3	52.9	64	52.0	73		
4'	14.2	43	3.6(1.1)	43.0	22.0	73	21.7	65	21.5	68	37.6	81	37.6(12)	81.1	58.0	78	57.6(18)	82.0	55.6	88	57.2	80		
5'	11.4	10	2.8(0.9)	12.0	16.3	29	17.4	33	17.9	31	34.9	39	35.3(8.3)	38.5	57.5	49	59.2(14)	51.7	47.8	45	60.6	54		

TABLE V
CALCULATED VALUES OF $F(n)$ FROM EXPERIMENTAL
DATA (TABLES III AND IV)

Batch no.	Hole diameter, 0.7 cm.					Hole diameter, 1.0 cm.				
	Screw, r.p.m.					Screw, r.p.m.				
	1	6	12	20	Average	1	6	12	20	Average
1'	0.0232	0.0242	0.0234	0.0191	0.0225	—	0.0354	0.0346	0.0380	0.0360
2'	—	0.0181	0.0174	0.0193	0.0183	0.0392	0.0278	0.0309	0.0293	0.0318
3'	0.0168	0.0174	0.0175	0.0170	0.0171	0.0290	0.0286	0.0308	0.0315	0.0300
4'	0.0229	0.0198	0.0192	0.0208	0.0207	—	0.0348	0.0337	0.0343	0.0342
5'	0.0238	0.0192	0.0196	0.0206	0.0206	0.0482	0.0384	0.0400	0.0364	0.0407
6'	0.0274	—	0.0286	0.0276	0.0279	0.0486	—	0.0489	0.0490	0.0488
7'	—	0.0178	0.0182	0.0168	0.0176	—	0.0295	0.0289	0.0328	0.0304
8'	0.0166	0.0163	0.0175	0.0182	0.0172	0.0282	0.0309	0.0336	0.0374	0.0309
9'	0.0203	0.0234	0.0223	0.0253	0.0230	0.0350	0.0439	0.0447	0.0416	0.0415
10'	0.0134	0.0139	0.0139	0.0151	0.0141	0.0224	0.0243	0.0241	0.0262	0.0242

where l is equal to 10 cm. and r_0 assumes the two values of 0.5 and 0.35 cm.; the factor 60 adjusts the flows, V , which are expressed in ml. per minute instead of in ml. per second.

In the same graph the values obtained from the extrusion data (Table V) and the ordinal number of the material are plotted. The considerations established for the tests of the first group of materials also apply here; so the experimental values never agree absolutely with the theoretical ones.

The results, however, confirm the data obtained analytically on the basis of the dimensions of the apparatus and of the rheometric parameters of the materials. In other words, for the extrusion from a cylindrical hole it is possible to determine, on the basis of the rheometric constants and the dimensions only, the relationship existing between flow and pressure difference from the equation which is valid within the limits of constants c and n .

$$P = K^n \sqrt{V} \quad (7)$$

$$\text{where } K = \frac{c}{F(n)}.$$

SUMMARY

A cylindrical rheometer of the Couette type, suitable for the experimental determination of the rheological properties of extruded materials, was designed to provide data which could not be obtained with existing plastometers. The purpose of this study was strictly practical, as the work was performed in connection with a study of extruders.

The results obtained on twenty-five different materials—natural and synthetic rubbers and compounds of both with various fillers—are reported; measurements fall within shear rate limits from 1 to 100 seconds⁻¹. In this interval the relationship between $\log D$ (rate of shear) and $\log \tau$ (shear stress) is nearly a straight line. It may, therefore, be analytically interpreted by the power law: $D = -(\tau/c)^n$, where n and c are parameters characteristic of the material. As the power law is known to be of limited validity, attempts were made to ascertain the limits of its application in laminar flow through a cylindrical hole. The results of measurements carried out on a 2-inch extruder and employing the same materials as were tested by the rheometer are reported. Measurements of pressure and flow were made, using discharge holes of various diameters and operating the screw at various speeds.

Reasonable agreement was found between values of flow and pressure determined with an extruder and those calculated from parameters n and c determined with the cylindrical rheometer.

ACKNOWLEDGMENT

The author is greatly indebted to Luigi Emanuelli for his helpful advice and encouragement and wishes to thank the Pirelli Società per Azioni for permission to publish this paper.

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X-RAY STUDY OF THE CRYSTALLIZATION OF VULCANIZED RUBBER DURING STRETCHING. II.*

V. I. KASOTOCHKIN AND B. V. LUKIN

INTRODUCTION

The physical-mechanical properties of rubber unquestionably depend upon its molecular structure. Properties of such practical importance as tensile strength, elasticity, and heat build-up are related to the nature of the rubber molecules, their activity, the character of their intermolecular bonds, and their spatial structure. The crystallization of vulcanized rubber on stretching also depends on the same molecular characteristics, and, as was shown in previous work¹, it is closely related to the physical-mechanical properties of the vulcanizate; consequently the crystallization and molecular reorientation of rubber are excellent indicators of a number of properties of rubber that are of practical importance. A study of the crystallization of vulcanized rubbers as a function of the time of vulcanization, sulfur content, accelerator content, and plasticizer content makes it possible to treat a number of these physical-mechanical properties on a molecular basis.

In earlier work² the crystalline phase of stretched specimens in relation to the time of vulcanization was studied. In this investigation, natural rubber mixtures containing 7 per cent of sulfur and also various accelerators were utilized. The maxima were indicated on the curves of crystal content as a function of the time of vulcanization for a given stress (the curves of crystal formation); these maxima corresponded to the maxima of the corresponding curves of tensile strength. The effects of accelerators such as thiuram, mercaptobenzothiazole, and diphenylguanidine were observed in the shift of the maximum to the region of the shortest time of vulcanization, as well as in the crystal content.

According to Dogadkin³, the changes in rubber which occur during vulcanization depend on a number of factors. These can be divided into chemical processes which are fundamentally opposed; the formation of intermolecular bonds by the action of the vulcanizing agent, and the disintegration of the chains by the action of molecular oxygen. The kinetic curves of these processes, when taken as a whole, give a kinetic curve of the tensile strength. These theories were developed by Dogadkin, Karmin, and Golberg³. The character of the tensile strength curve was taken into consideration by the authors in interpreting the crystallization curves, and the results obtained were explained on the basis of two fundamental processes which take place during vulcanization: first, the formation of a cross-linked structure in the reaction between rubber and sulfur, and, secondly, oxidative destruction of the rubber. However, these processes are obviously insufficient to explain the nature of crystallization, which is expressed by the specific course of this

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Journal of Technical Physics*, Vol. 19, No. 1, pages 76-83, January 1949.

Ingredients	MIXTURES STUDIED							
	No.	V	VI	VII	VIII	IX	X	XI
Smoked sheet	100	100	100	100	100	100	100	100
Sulfur	—	2	2	2	2	7	7	7
Zinc oxide	—	5	5	5	5	5	5	5
Stearic acid	—	2	2	2	2	2	2	2
Mercaptobenzothiazole	—	0.6	—	—	—	0.3	0.3	0.3
Diphenylguanidine	—	—	—	0.756	—	—	—	—
Thiuram	—	—	—	—	0.854	—	—	—
Dibutyl phthalate	—	—	—	—	—	—	30	—
Mazut	—	—	—	—	—	—	—	30

curve in the first phase of vulcanization up to the optimum, as well as in the second phase beyond the optimum, for different vulcanized mixtures. The purpose of the present investigation was to study in more detail the crystallization curves of vulcanization in relation to the elongation of vulcanized mixtures.

The mixtures studied are given in the accompanying Table.

The methods of preparation of the mixtures, their vulcanization, and the making of x-ray diagrams were described in the preceding work¹, and these methods were not changed materially in the present study.

The proportions of crystalline phase were calculated by the method of Field. This method, however, does not give consistent values of the absolute quantity of crystalline phase.

This method of measurement of the proportion of crystalline phase was adopted in toto, since mathematical errors in the measurement of the absolute quantity of the crystalline phase can be determined only on the ordinate scale, and they cannot be estimated from the general shape of the curves of crystallization.

EFFECT OF OXIDATIVE DESTRUCTION ON CRYSTALLIZATION OF SMOKED SHEET RUBBER

Standard smoked sheet rubber (Mixture V) was heated in a vulcanization press without previous plasticization or addition of any ingredient. The conditions of heating were the same as those used by Lukin and Kasatochkin¹ for vulcanizing the earlier mixtures, i.e., in a millimetric press at 143° C.

In Figure 1, Curve 1 shows the crystal content of specimens of smoked sheet, stretched 500 per cent, as a function of the time of heating. It is evident

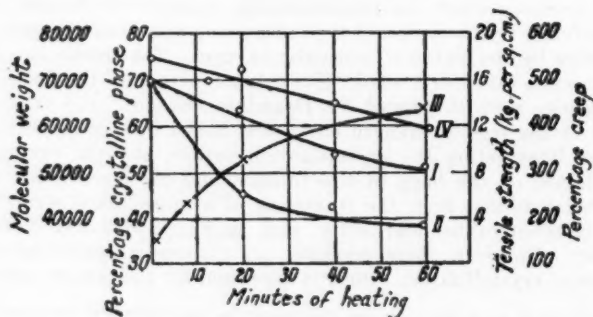


FIG. 1.—Changes of properties of smoked sheet rubber during heating. I. Crystal formation; II. Molecular weight; III. Creep; IV. Tensile strength.

that the quantity of crystals decreased sharply as heating progressed. In this experiment the effect of oxidative destruction on the tendency of the vulcanizate to crystallize is evident.

Together with the change of crystal content, the molecular weights of the samples of rubber were computed at various stages of heating by determining the changes of viscosity of dilute solutions. The changes of molecular weight are shown in Figure 1, Curve 2. This curve shows that the molecular weight of rubber also decreases as heating progresses. Presumably in addition to the decrease of molecular weight during heating, there is an accumulation of low molecular oxidation products which undoubtedly influence the tendency of the rubber to crystallize during stretching. This governs the creep of the specimens. The changes of creep are shown in Figure 1, Curve 3. Creep was measured at a stress of 1 kg. per sq. cm. at 18° C for 50 hours.

Figure 1, Curve 4, shows the changes in tensile strength.

CRYSTALLIZATION OF VULCANIZATES CONTAINING 2 PER CENT SULFUR

The change of crystallization of vulcanizates containing relatively small percentages of sulfur is of great interest, since in this case at the optimum point of vulcanization the amount of bound sulfur reaches more than 1.9 per cent (Figure 8). From this it may be assumed that, in the later stages of vulcanization, the number of sulfur bridges does not appreciably increase, and the vulcanization process continues in a network of constant density.

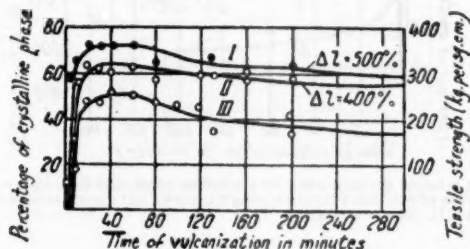


FIG. 2.—Relation between the proportion of crystalline phase and between the tensile strength and the time of vulcanization of Mixture VI containing 2 per cent sulfur and mercaptobenzothiazole as accelerator. I and II. Crystal formation; III. Tensile strength.

Figures 2, 3 and 4 show the curves of crystallization of Mixtures VI, VII and VIII when stretched 400 and 500 per cent, and the corresponding tensile strength curves.

A comparison of the measured sulfur content of Mixtures VI and VII with the mixtures described earlier containing the accelerators, but also a higher percentage of sulfur (7 per cent) is interesting, and, by such a comparison it is possible to estimate the influence of sulfur on the crystallization process.

Figure 5 shows, in comparison, the curves of crystallization for Mixtures II and VI containing 7 and 2 per cent of sulfur, respectively, with mercaptobenzothiazole as accelerator. A comparison of these curves shows that the decrease of the sulfur content is evident in the character of the maximum point as well as by its position. In the curve for Mixture VI, containing 2 per cent of sulfur, there is a broad maximum, whereas for Mixture II containing 7 per cent of sulfur, the maximum is sharp.

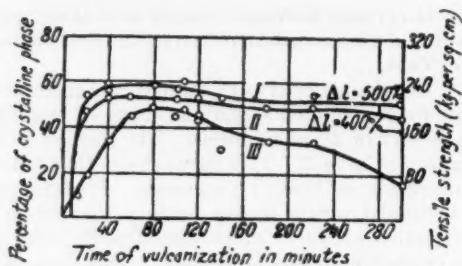


FIG. 3.—Relation between the proportion of crystalline phase between the tensile strength and the time of vulcanization of Mixture VII containing 2 per cent sulfur and diphenylguanidine as accelerator. I and II. Crystal formation; III. Tensile strength.

Furthermore, a displacement of the maximum for Mixture VI to the region of the longest times of vulcanization and a decrease of the crystal content in comparison with Mixture II also are evident. Mixture II shows a sharply decreased crystal content beyond the maximum, whereas the decrease in Mixture VI is relatively small.

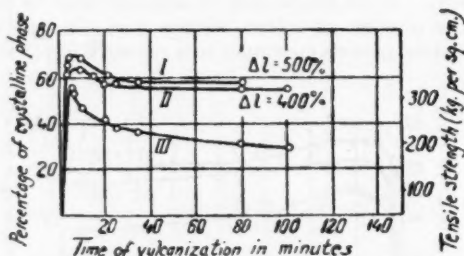


FIG. 4.—Relation between the proportion of crystalline phase and between the tensile strength and the time of vulcanization of Mixture VIII containing 2 per cent sulfur and thiuram as accelerator. I and II. Crystal formation; III. Tensile strength.

A very important factor which influences the decrease of the crystalline phase is the progressively increasing proportion of sulfur bridges which unite the rubber molecules and reduce their mobility. For mixtures containing a relatively small sulfur content, when the process of chain formation reaches

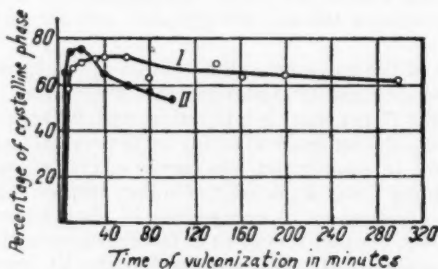


FIG. 5.—Relation between the proportion of crystalline phase and time of vulcanization of Mixtures II and VI, containing mercaptobenzothiazole, for an elongation of 500 per cent. I. 2 per cent sulfur; II. 7 per cent sulfur.

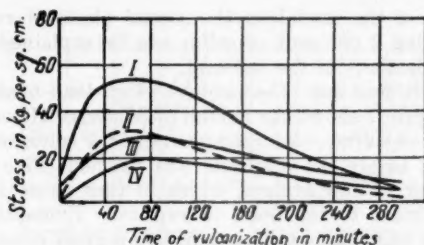


FIG. 6.—Strain moduli for mixtures containing 2 per cent of sulfur, and elongated 400 per cent and 500 per cent, respectively. I and II. Mixture VI containing mercaptobenzothiazole. III and IV. Mixture VII containing diphenylguanidine.

the optimum point, this factor can have no great significance in the process of crystal formation during the second phase of vulcanization.

In this case, a satisfactory explanation of the decreased crystal content and decreased tensile strength beyond the optimum point of vulcanization is

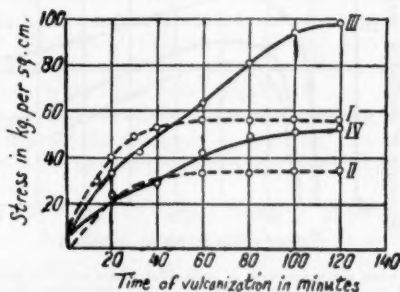


FIG. 7.—Strain moduli for mixtures containing 7 per cent of sulfur, and elongated 400 per cent and 500 per cent, respectively. I and II. Mixture II containing mercaptobenzothiazole; III and IV. Mixture II containing diphenylguanidine.

that the oxidation products have a plasticizing action on the rubber. One of the fundamental effects of this plasticizing action of the oxidation products and, consequently, the increased plasticity of the material, is the character of the moduli. Figure 6 shows the moduli at 400 and 500 per cent for Mixtures VI and VII.

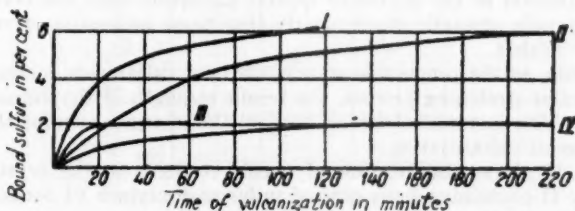


FIG. 8.—Kinetics of formation of bound sulfur. I. Mixture II containing 7 per cent of sulfur and mercaptobenzothiazole; II. Mixture III containing 7 per cent of sulfur and diphenylguanidine; III Mixture VI containing 2 per cent of sulfur and mercaptobenzothiazole; IV. Mixture VII containing 2 per cent of sulfur and diphenylguanidine.

The decrease of the moduli in the second phase of vulcanization in the mixtures containing 2 per cent of sulfur can be explained only on the basis of an increased plasticity of the material.

It is difficult to find any other factors which tend to decrease the moduli in this case. Figure 7 shows the moduli of Mixtures III and IV¹, which contained 7 per cent of sulfur. A large amount of the sulfur, only 3 to 4 per cent of which reacted before the optimum was reached (Figure 8), produces an increasing number of new bridges, which in turn cause a constant increase of the moduli almost to the point of rupture. Evidently in this case the decreased crystal content may be ascribed to a great extent to the decreased mobility of the molecular chains and to the progressively increasing density of the spatial network.

Figure 9 shows the curves of crystallization of Mixtures IX, X and XI containing 30 per cent of the plasticizers dibutyl phthalate and Ishimbayev mazut (mineral oil) and, for comparison, the curve for the same mixture containing no plasticizer.

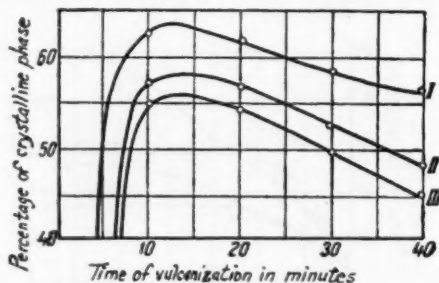


FIG. 9.—Relation between the proportion of crystalline phase and the time of vulcanization for mixtures containing plasticizers. I. Mixture IX containing no plasticizer; II. Mixture IX containing 30 per cent of; III. Mixture X containing 30 per cent of dibutyl phthalate.

As was expected, the plasticizers reduced the number of crystals formed during stretching of a vulcanizate 500 per cent for all states of vulcanization. It is of interest to note that dibutyl phthalate reduced the crystal content somewhat less than does Ishimbayev mazut. This seems to explain the characteristic effect of this substance as a plasticizer.

CRYSTAL FORMATION AND TENSILE STRENGTH

A comparison of the curves of crystal formation with the corresponding curves of tensile strength shows clearly that these properties of vulcanizates are closely related.

As a rule, as the proportion of crystals in a vulcanizate increases during any particular stretching process, the tensile strength of the vulcanizate also increases. This fact was observed with all the mixtures studied through the entire range of vulcanization.

Figure 10 shows the relation of tensile strength to the crystal content of Mixture II containing 7 per cent of sulfur and mixture VI containing 2 per cent of sulfur for the entire range of vulcanization.

The graphs show clearly the identical changes of the two above-mentioned properties of the vulcanizates, and also that the tensile strength is a function

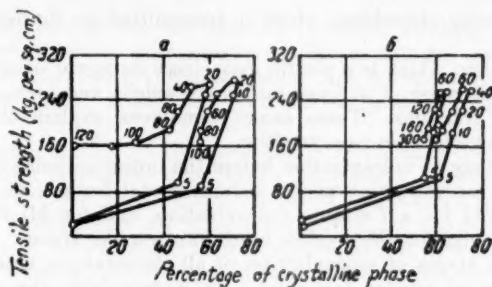


FIG. 10.—Relation between the tensile strength and proportion of crystalline phase for the entire range of vulcanization. The figures on the curves show the vulcanization times in minutes. a. Mixture II containing 7 per cent of sulfur and mercaptobenzenothiasole; b. Mixture VI containing 2 per cent of sulfur and mercaptobenzenothiasole.

of the crystal content. This function is a dual one, i.e., has two values for the tensile strength, one of which corresponds to the first phase of vulcanization before the optimum point, and the other to the second phase after the optimum point, both corresponding to a single crystal content for every mixture.

For example, for Mixture II (Figure 10) 47 per cent of the crystals correspond to a tensile strength of 90 kg. per sq. cm. for a 5-minute vulcanizate and 222 kg. per sq. cm. for a 70-minute vulcanizate.

The dual nature of this function is, in our opinion, an indication of the different nature of the tensile strength in the two phases of vulcanization. The graphs shown in these figures are interesting in this connection, since they emphasize this difference.

A comparison of the values of tensile strength, measured at the optimum state of vulcanization, for the different mixtures with their crystal contents at the optimum points proves the regularity of the increase of tensile strength with increase of crystal content.

Figure 11 shows this relationship for the twelve mixtures studied.

INTERPRETATION OF THE RESULTS

Unvulcanized unplasticized rubber has a high power of crystallization. The usual interpretation of this fact, which involves the high molecular weight of the rubber, leads to the hypothesis that chains are formed by the application

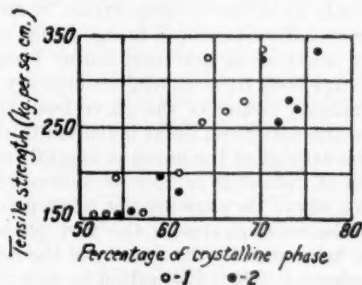


FIG. 11.—Relation between tensile strength and proportion of crystalline phase for twelve mixtures of various compositions at the optimum point. 1. Elongated 400 per cent; 2. Elongated 500 per cent.

of a stress during stretching, which is transmitted to the entire volume of the specimen.

Milled rubber, which is a plastic mass, loses its power of crystallization as a result of a decrease of average molecular weight and increased content of low-molecular fractions. These same phenomena explain the lack of any tendency of raw mixtures to crystallize.

The first stage of vulcanization before the optimum point is characterized first of all by an induction period before crystal formation. For example, for Mixture VII for a 7-minute vulcanization, and for Mixture VIII for a 4-minute vulcanization the crystals hardly form under stress.

In the last stages of vulcanization of all the mixtures studied, there is a rapid increase of crystal formation. In approaching the optimum state of vulcanization, the crystal formation curves show a smooth course which is characteristic for each mixture.

The cause of the peculiar course of the curves of crystal formation is without doubt the complex molecular mechanism of the vulcanization process. We shall depart from the usual theories of the formation of sulfur bridges between the molecular chains during the reaction of the rubber with the sulfur.

As these studies show (see Figure 8), the proportion of bound sulfur increases from the beginning of vulcanization, but the mixture remains plastic, and, consequently, still shows a tendency to flow during stretching. It may be that, during this period, there is present a certain quantity of aggregates, that is, of segments of newly formed special networks, but the complete spatial network has not really been formed at this point. The structure of the whole spatial network can be considered as completed after the aggregates are finally united by sulfur bridges. This assumption helps us to understand that, in the region of the rapidly rising curve of crystal formation, very small changes in the percentage of bound sulfur and, correspondingly, of the relaxation time, sharply increase the quantity of crystals.

The appearance of the spatial network coincides with the end of the induction period. For different mixtures, the quantity of bound sulfur corresponding to the end of the induction period varies; consequently, the moment when the whole spatial network has been formed corresponds to different proportions of bound sulfur with different mixtures. It would be added that, with a uniform distribution of bridge sulfur, the end of the induction period, in other words, the beginning of the crystal-formation curve, must correspond to the determined quantity of bridge sulfur for all the mixtures.

The fact that the beginning of the curve of crystal formation for the different mixtures corresponds to different proportions of bound sulfur seems to attest to either an unequal distribution of bridge sulfur or to different proportions of bound sulfur which does not form sulfur bridges in the different mixtures. It follows that both these conditions actually occur.

Apparently the changing course of the curve from the moment when the rapid increase stops to the maximum point is related to the distribution of the sulfur bridges. At this section of the curve of crystal formation, an equalization of the distribution of the sulfur bridges because of the easier formation of these bridges in regions where they are sparser takes place.

Crystallization of the vulcanizates in the first phase after the optimum point also is doubtless influenced by the density of the network, which reduces the mobility of the molecules. It is interesting to note that a relatively sharp decrease of the proportion of crystals during the vulcanization process takes place in mixtures with relatively high sulfur contents. In these cases a

disparity is observed between the decrease of tensile strength and decrease of crystal formation, which is especially notable at 400 per cent elongation. For example, for Mixture II vulcanized more than 60 minutes and stretched 400 per cent, no crystals are evident, but the tensile strength is 230 kg. per sq. cm.

From the point of view of the molecular mechanism of tensile strength, vulcanizates which crystallize most nearly completely possess high tensile strengths, thanks to the large number of chains which carry the stress. In noncrystallizing vulcanizates, the orientation chains play the same role.

The presence of bound sulfur hinders crystallization because of the non-correspondence between the C-S bond and the periods in the crystalline lattice of the rubber. Non-bridge sulfur does not have any essential effect on the mobility of the molecules and, consequently, does not influence the process of orientation of a chain along the direction of stretching. However, the chains which are occupied by non-bridge sulfur cannot play any part in the crystallization process, and this causes a corresponding decrease of the power of crystallization.

In the second phase of vulcanization in an insufficiently dense network when the mobility of the molecules is not yet sufficiently restricted and the vulcanizate still possesses elasticity and high tensile strength, the molecules may lose the power of crystallization as a result of the large proportion of bound sulfur. This explains the disparity between the curve of crystal formation and the tensile strength curve in the vulcanization process for mixtures with high sulfur contents.

It may be assumed that the course of the crystallization curve in the second phase of vulcanization also is influenced by the degree of unequal distribution of sulfur bridges. In fact, when the distribution of the sulfur bridges inside the separate aggregates is not uniform, most of those segments which are in a position to form sulfur bridges react, and most of the sulfur in the aggregates reacts, forming non-bridge bound sulfur. This causes a generally increased amount of bound non-bridge sulfur, with a corresponding decrease of the power of crystallization for a relatively small change of tensile strength.

CONCLUSIONS

1. The relation between the crystal content of stretched vulcanizates to the time of vulcanization for different mixtures of natural rubber was studied by the x-ray method.
2. It was shown that the tensile strength is a function of the crystal content of the stretched vulcanizate and of the total time of vulcanization.
3. The nature of crystal formation depends on the following factors: changes of density of the network of sulfur bridges, their distribution, the degree of oxidative destruction, and the quantity of bound sulfur which has not formed bridges between the molecular chains.

ACKNOWLEDGMENT

We express our gratitude to Professor B. A. Dogadkin and to B. K. Karmin for their interest in our work and for their valuable comments.

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CRYSTALLIZATION IN UNSTRETCHED RUBBER MICROSCOPIC STUDY IN POLARIZED LIGHT *

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There is considerable interest in the crystallization of rubbers, both from the practical and the theoretical points of view. In the first place, crystallization of raw rubber causes inconvenience in rubber processing and crystallization in the finished product severely limits its usefulness at low temperatures. Secondly, knowledge of degree and rate of crystallization as a function of molecular structure is of great importance in designing synthetic elastomers and in developing theories of their stress-strain relationships and other physical properties.

Most studies of the crystallization of rubbers have been made by observing changes in volume by dilatometer methods¹ or by x-ray diffraction. Some study has been made of rubber crystals obtained from solution².

The x-ray diffraction method is not very sensitive in detecting small amounts of crystallinity, chiefly because the crystals are so imperfect. Some elastomers which show considerable volume change in the dilatometer³ show just perceptible x-ray effects⁴. Consequently it was considered advisable to study crystallization by direct microscopic examination.

PROCEDURE

The method consisted of freezing thin films of elastomers at about -25°C for varying lengths of time and then photographing them with a polarizing microscope. The cold stage consisted essentially of a glass vessel 3.5 inches in diameter by 1.5 inches deep, with a double evacuated bottom. This vessel contained an antifreeze mixture and a cooling coil consisting of about ten turns of $\frac{3}{16}$ -inch copper tubing. The samples were in the form of thin films laid down on microscope slides, covered with regular cover glasses, and waterproofed by cementing their edges. These were laid flat on the bottom of the vessel. The cooling coil was supported independently of the microscope to allow rotation of the stage, vessel, and sample together. The temperature was regulated by pumping cold acetone through the coil from a commercial refrigerating unit, so that temperatures down to -20°C could be maintained indefinitely.

The microscope objective was a Zeiss 40 \times , 0.75NA, 4.3 mm. achromat corrected for water immersion. The antifreeze solution was a mixture of water 55, ethyleneglycol 30, and alcohol, 15. This mixture has a low enough freezing point; it dissolved ice crystals condensed from the atmosphere; it was sufficiently mobile; and its refractive index was not far enough from that of water to affect seriously the performance of the water immersion objective. One of the old type objectives corrected for glycerol immersion would be more suitable for this work, but such lenses seem to be no longer available. The microscope

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 413-415, February 1950. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its International Meeting in Cleveland, Ohio, October 11-13, 1950. The work was carried out under the sponsorship of the Chemicals and Plastics Section, Research and Development Branch, Office of the Quartermaster-General.

objective was thermally insulated from the body tube of the microscope by means of an extension collar, about an inch long, made of machined plastic.

This arrangement permitted observations through indefinite periods of time. Difficulty was experienced by moisture condensing on the back lens surface of the objective. Consequently the objective had to be removed and its rear surface dried off about once an hour during continuous observations.

RESULTS

Figures 1, 2, and 3 show the progress of crystallization with time. The sample is a film of raw rubber 0.5 to 1 micron thick prepared by dipping a microscope slide in diluted Hevea latex and drying. Photographs of the same field were taken after 24, 48, and 96 hours at -25°C . The chief characteristic is the formation of spherulites due to needlelike crystals growing out from

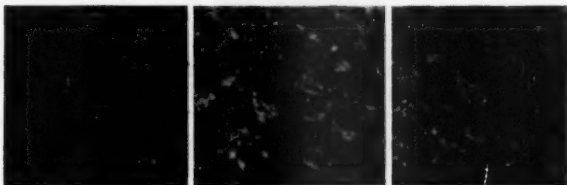


FIG. 1.—24 hours.

FIG. 2.—48 hours.

FIG. 3.—96 hours.

Rubber frozen at -25°C (750 \times).

nuclei. These spherulites are considerably flattened, since the sample thickness was less than their diameter. All nuclei are not formed at once, but new ones keep appearing as time progresses. The rate of crystallization is thus strongly affected by the rate of nucleus formation as well as by the rate of crystal growth. In Figure 3, where crystallization has proceeded practically to completion, the spherulites seem to fill all the space available, and the sample has the superficial appearance of being completely crystallized.

Figures 4, 5, and 6 show the effects of melting and refreezing a sample of rubber. Figure 4 is a fresh sample frozen 3 days at -25°C . Figure 5 is the same field after the sample had been melted at room temperature and refrozen for 3 days at -25°C , and Figure 6 is the same field after subsequent melting at 40°C and refreezing at -25°C for 4 days. In Figure 5 the pattern of Figure 4 is repeated. Not only are the same clusters reformed, but the detailed structure of individual clusters is reproduced with striking fidelity. Thus, even though the crystals melt well below room temperature, the motion of the

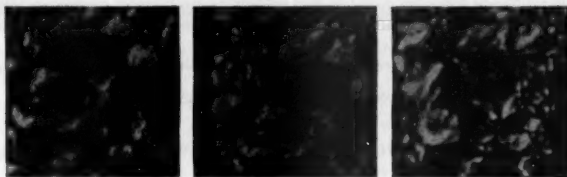


FIG. 4.—Original crystallization, 72 hours at -25°C .

FIG. 5.—Refrozen after melting at 20°C .

FIG. 6.—Refrozen after melting at 40°C .

Rubber refrozen at -25°C (750 \times).

molecular segments is so restricted at room temperature that on refreezing the same crystal pattern is renewed. Figure 6 shows the same pattern on the left part of the field but a different pattern on the right, indicating that some changes have taken place on heating to 40° C.

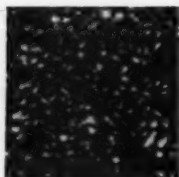


FIG. 7.—Original crystallization.



FIG. 8.—Refrozen after melting at 12° C.

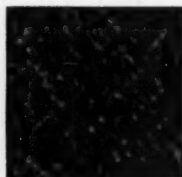


FIG. 9.—Refrozen after melting at 20° C.

Polybutadiene refrozen at -25° C (750X).

Figures 7, 8, and 9 show the same effect in a sample of polybutadiene. This is a sample polymerized at 41° F and presumed from dilatometer studies to crystallize readily, although only slight evidence of crystallinity was observed by *x*-ray diffraction. [It is comparable to material studied by Lucas, Johnson, Wakefield, and Johnson³ and by Beu, Fryling, and McMurry⁴.] Here also the crystal pattern is reproduced after melting at 12° C but not after remelting at 20° C. The crystal clusters are much smaller than in rubber, and individual spherulites are difficult to identify.

Although, in general, melted and refrozen samples tended to reproduce the same crystal pattern, a number of inconsistent results were obtained which indicated that the previous history of the sample had an effect on its crystallization. Consequently a sample was submitted to repeated cycles of melting at 20° C and freezing at -25° C. Figures 10, 11, 12, and 13 show part of this series. These represent the same field in the sample after the original freezing and after the first, second, and fifth cycle. This is the same sample as Figures 1, 2, and 3, which are the sixth cycle of this series. Only pictures after 24 hours are shown as they accentuate the differences. There is a considerable change in detail of the pattern on the first cycle, but the differences tend to disappear

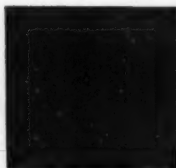


FIG. 10.—First freezing.

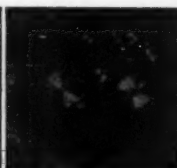


FIG. 11.—First refreezing.

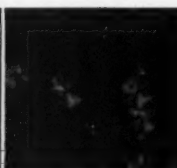


FIG. 12.—Second refreezing.



FIG. 13.—Fifth refreezing.

Refrozen rubber, 24-hour periods at -25° C (750X).

with subsequent cycles. Exactly similar results were obtained on samples of cured rubber except that the cured samples froze at a slower rate. Repeated remelting at a temperature of 60° C resulted in poor reproduction of the patterns.

Figure 14 is a large spherulite in polychloroprene showing the change in the appearance on rotating the Nicol prisms. This sample was thick relative to the diameter of the spherulite, so it was probably not flattened. The general appearance is the same as that observed with convergent polarized light in a single biaxial crystal and known to petrographers as the "directions image", "conoscopic view", or "interference pattern"⁶. It seems reasonable to expect

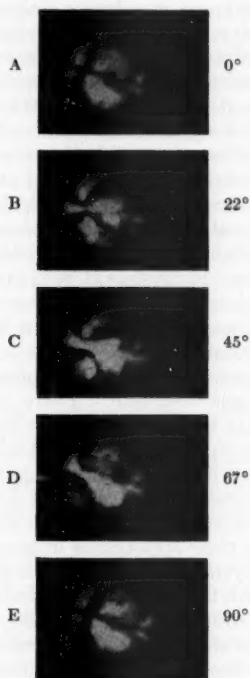


FIG. 14.—Neoprene (1000 \times). Single spherulite showing effect of rotating Nicol prisms

effects, in radiating crystals in parallel light, similar to those observed with a single crystal in converging light⁴.

DISCUSSION

These results indicate that direct microscopic examination is a more positive qualitative test for crystallinity in high molecular-weight polymers than is *x*-ray diffraction. Materials such as rubber and polychloroprene have long ago been shown to be crystalline by *x*-ray diffraction. However, in most of the newly developed cold rubbers, appreciable amounts of crystallinity have not been detectable by *x*-ray diffraction except in low temperature polybutadiene⁷. *x*-Ray diffraction has not shown crystallinity in polybutadienes polymerized at higher temperatures nor in copolymers of styrene and butadiene of the GR-S type, even when polymerized at low temperatures. On the other

hand, dilatometer studies show first-order transitions in these materials, large changes for low-temperature polybutadiene, and small changes for some low-temperature copolymers⁵.

Figure 4 shows a considerable amount of crystallization in a polybutadiene polymerized at 41° F. Photographs have been taken of other polymers: regular GR-S showed no evidence of crystallization even after weeks at -30° C. Two other polymers—one a polybutadiene polymerized at 122° F, the other a 90:10 butadiene-styrene copolymer polymerized at 41° F—showed small amounts of crystallinity. Neither of these samples showed any evidence of crystallinity by x-ray diffraction at temperatures down to -50° C, but did show small first-order transitions in the dilatometer. Since the microscopic method is not quantitative, it would seem that the dilatometer offers the most promising method of making crystallinity studies of elastomers.

It is possible that the effects seen with the microscope are not due to true crystallization. Local orientation and alignment of long chains would produce regions showing birefringence. However, such high degree of orientation would have the same practical effect on the physical properties as true crystallization. Furthermore, such orientation is essentially imperfect crystallization. All high polymers form imperfect crystals at best, and undoubtedly the inability of x-ray diffraction to detect crystallization in these samples is due to the higher degree of imperfection in these materials than in less imperfect crystals, such as natural rubber and polyamides.

It is quite certain that, even under the best possible conditions, crystallization of a high polymer is not complete. There has been some difference of opinion in the literature as to the degree of crystallization obtainable in rubber. However, it is probable that in rubber the crystallinity is not much greater than 25 to 30 per cent⁶. In Figure 3 the spherulites apparently fill all of the available space. Hence, the spherulites themselves must actually contain more amorphous material than crystalline. Although the crystallites are not resolved, there can be no doubt from their appearance in polarized light that the spherulites consist of needlelike crystals radiating from a nucleus. Comparison of the sign of the birefringence with that of crystals formed by stretching rubber show that the rubber chains are oriented perpendicularly to the axes of the crystals, that is, the molecular chains are arranged tangentially in the spherulite. The picture of the spherulite is, therefore, somewhat like a ball of string where there are radial regions of similar orientation which form crystals and regions between these crystals where the chains are not parallel, that is, amorphous regions.

It does not appear feasible to make quantitative measurements of birefringence under these circumstances, although Brenschede⁷ has tried it with some polyamides. The magnitude of the retardation is very low first because of the fact that the cluster is only partly crystalline and secondly, in these pictures, the clusters are not complete spheres.

The photographs of the Neoprene cluster show an interesting effect. If the appearance can be justifiably interpreted as a biaxial directions image, some deductions as to crystal orientation are possible. The crystal is known from x-ray diffraction to be orthorhombic. The B axis is the direction of the molecular chains and the greatest refractive index. The sign of the double refraction in the cluster shows this axis to be oriented tangentially. The definite biaxial appearance of the dark bands indicates orientation of some higher order, probably with the B axis constrained to be parallel to a plane. In the spherulite on

the left in Figure 14 the vertical dark bar in the zero orientation picture is the trace of this plane on the sphere. The distance between the hyperbolas in Figure 14C is a measure of the optic angle. A comparison of Neoprene with rubber shows either that the rubber crystal must be nearly uniaxial⁹, or there is random orientation of the B axis in the spherulites.

When the cluster is in or near the 45° position, the two small quadrants would not be very prominent if the cluster were small and the retardation low. This would account for the general appearance of the polybutadiene pictures. Uniaxial spherulites have been shown in polyamides⁷ and in medium molecular weight polyesters in this laboratory. It seems, therefore, that all linear high polymers tend to crystallize in a similar way—spherulitic clusters of radiating needlelike crystals with the molecular chains in a tangential direction in the spherulite. The higher order orientation has so far only been observed in polychloroprene.

The reproducibility of the crystal pattern on refreezing illustrated in Figures 10 to 13 is of considerable interest in connection with theories of retractive force in stretched elastomers. In view of these results, the following picture of the mobility of polymer chains is probably justified:

In a sample of polymer (at room temperature) which has come to an essentially steady state, the chains do not move or migrate to any extent compared to the range of forces involved in crystallization, since recrystallization brings the same molecular segments back into essentially the same crystal configuration. However, when a sample is first formed, the molecular segments are not necessarily in their most favored configuration. Thus on the first cycles, minor changes of configuration take place before they settle down to the preferred state; after this, practically no further changes occur on subsequent cycles. This would explain the changes in crystal pattern observed on the first refreezing and such well known effects as the higher modulus of rubber on its first cycle of elongation.

Current theories¹⁰ as to the mechanism of the retractive force usually postulate considerable freedom of the molecular segments. The observations reported here indicate severe restrictions of motion at room temperature. These restrictions are reduced at higher temperatures and may not be important above about 60° C in rubber. It has not been possible by these experiments to estimate the maximum motion permitted.

SUMMARY

Since many elastomers indicate by their physical properties that crystallization occurs even when such crystallization is not detectable by x-ray diffraction, a direct microscopic study in polarized light was undertaken.

This study confirms the presence of such crystallinity not only in rubber but also in polybutadiene and some low-temperature copolymers. Furthermore, the same crystal pattern is reproduced on melting and refreezing provided the intermediate melting temperature is not too high.

This indicates that x-ray diffraction is not a very sensitive method for detecting small amounts of crystallinity in high polymers. The reproduction of the crystal pattern on refreezing shows that the molecular segments have limited mobility even at room temperature; this may require revision of current theories of the origin of retractive forces in elastomers.

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OPTICAL EXAMINATIONS OF ANISOTROPY IN VULCANIZATES *

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A vulcanized rubber is frequently anisotropic. The different values of modulus, tensile and tear strength, swelling in solvents, shrinkage after vulcanization, and electrical properties, according to the direction along which the tests are carried out, are well known. Anisotropy can also be examined in other ways, and this report illustrates how interesting optical examinations of anisotropy in vulcanized rubbers can be made, completing and defining the results obtained by other means.

Dawson and Porritt¹, dealing with grain, distinguish the effect caused in rubber alone from that obtained when elongated particles are present.

The grain is formed during those processes of manufacture which deform the stock in a definite direction, such as mixing on rolls, calendering, and extruding. Hot rubber deformed in this way and then cooled unequally, on one face only, for example, or cooled after anchoring to a fabric liner, takes up a condition of internal strain. This grained unvulcanized stock may result in the vulcanized rubber retaining some of the grain. Further, rubber stock containing compound ingredients of an acicular type, such as clay, light magnesium carbonate, and tripoli, have the particles of the fillers aligned with their longest dimensions parallel to the direction of travel of the rubber, resulting in marked development of grain. In general, very little of the grain due to the rubber phase survives hot vulcanization, but that arising from fillers always remains.

Gurney and Gough² have shown that movements in a raw compound take place in the mold during the first stages of vulcanization, and that the consequences of these movements, so far as anisotropy is concerned, are in fact more important than those which derive from calendering. The beginning of vulcanization fixes the rubber which has only just stopped moving during molding, or which is still moving owing to the retarded thermal expansion of internal parts. In such cases, anisotropy may occur in the rubber phase alone, but when acicular particles of compounding ingredients are present their orientation is an obvious consequence.

Scott³ points out that following flow, suitably exaggerated, during molding, "the dielectric constant and dissipation factors are, for some mixtures, different in the direction of flow and in the two mutually perpendicular directions. Results are consistent with the hypothesis that the filler particles are oriented in the rubber matrix". Here we see again underlined the effects of flow in molding, and the influence of the pigments.

The photoelastic properties of rubber, that is, double refraction as a function of strain, have been very carefully studied; it would appear, however, that double refraction in the absence of external stress due to previous deformations in the unvulcanized or semivulcanized state has been examined to a lesser degree.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 393-398, February 1951. This paper was presented at the International Meeting of the Division of Rubber Chemistry of the American Chemical Society, Cleveland, Ohio, October 11-13, 1950.

Ames⁴ briefly examined the double refraction of raw calendered rubber and its disappearance during recovery by thermal treatment.

Hurry and Chalmers⁵, dealing with photoelastic applications in the technology of rubber, mentioned the examination of movements of the material in the process of injection molding, but did not develop the theme.

Kruse⁶ examined through crossed Nicols transparent rubbers in which, when scorching had taken place, a plastic flow and successive relaxation were provoked. His examination was, however, conducted with thermal treatments rather far removed from those employed in the process of vulcanization, and concerned more with the mechanism of vulcanization than with the appearance of anisotropy in technical operations.

In the field of plastic materials, cases have recently been cited of examinations made under polarized light for the purpose of revealing or measuring double refraction as a result of molding⁷ or in calendering⁸.

The examinations described in this report illustrate typical and current cases of anisotropy existing in vulcanized rubbers produced in the laboratory, and which can be examined optically—anisotropy in the rubber phase alone due to flow at the beginning of vulcanization, and that due to orientation of the pigment particles following calendering or injection molding.

PREPARATION OF SAMPLES

Vulcanized rubbers prepared according to the following formulas have been used for general optical examinations of anisotropy, the observation of specimens 30 to 50 microns thick under the microscope, and the free observation of specimens a few millimeters thick.

Compounds	A	B	C	D	E
Smoked sheet rubber	100	100	100	100	100
Sulfur	2	2	2	2.7	2.7
Mercaptobenzothiazole	0.5	0.5	0.5	0.7	0.7
Diphenylguanidine	0.5	0.5	0.5	—	—
Zinc oxide	1	1	1	1	1
Stearic acid	1.5	1.5	1.5	1.5	1.5
MPC carbon black	—	1	—	—	1
Talc	—	—	1-15	—	—

Compound A is used preferably for macroscopic examinations, and should show the anisotropic behavior of the rubber phase alone; Compound B is used in microscopic examinations, as it is too opaque for thicker specimens; more detailed data can, however, be obtained with it. With C, containing some talc, it is possible to observe the orientation of the particles of the fillers, and to determine the anisotropy due to it, independently of that which occurs in the rubber phase alone. With magnesium carbonate and clay in fair percentages, it is not possible to make useful examinations, even if thin sections are used. Colloidal silica can, however, be adopted for loading, as it only slightly influences the transparency.

Compounds D and E differ from A and B only in the initial speed of vulcanization and risk of scorching.

Whereas it is possible to make a direct examination between crossed polaroids of sheets or articles of Compound A up to 4 mm. thick, sections about 1 to 2 mm. thick can be obtained from vulcanized products of any dimensions made with this compound, instead of with the production compound. The sections are cut with a rotating blade liberally wetted with soap and water.

The sections for microscopic examinations are obtained by immersing the vulcanized specimen in paraffin, cooling it with dry ice, and cutting it with a microtome. They are mounted in castor oil, which does not cause the rubber to swell and allows easy relaxation from occasional stresses due to mounting. The examination is made under a not very powerful microscope, with crossed Nicols. To obtain the outlines of the photographed objects the Nicols may be only partly crossed.

OPTICAL EXAMINATIONS

The first microscopic examinations of anisotropy in vulcanized rubbers were made on thin sections cut from rubber disks where mold overflow (spew) was also present; the double-refractive characteristics of this latter, noticed on various occasions, made advisable a more frequent and systematic examination of the overflow and of the areas near it.

A mold was built in which a slab of rubber measuring $20 \times 20 \times 0.4$ cm. can be vulcanized; the upper wall of the mold has fifteen openings in groups of three, in five rows, measuring 2×0.05 cm.; from these the rubber can flow into cavities at the back. If a slight excess of rubber is loaded into the mold, there is a movement of the rubber when the mold is closing and when the temperature rises, which does not altogether cease, or has only just ceased, when vulcanization commences; this movement is at its maximum near and inside the opening.

Let us consider in particular what happens in the case of a transparent compound, made according to Formula A. Figure 1, A, shows a part of the slab or rubber between crossed polaroids; after 60-minute vulcanization at the relatively low temperature of 120°C , the brilliant traces of the openings through which rubber has flowed can be seen, but the double refraction is not the same at all the openings, and is on the whole strictly localized in the regions of greatest movement. If, on the other hand, vulcanization takes place at the much higher temperature of 151°C for 10 minutes, the specimen between the crossed polaroids shows a more intense and widespread double refraction. In some cases the most intense double refraction is not localized under the opening but is slightly displaced to one side of it. Figure 1, B, shows, with respect to the preceding case, the effect of more rapid scorching in fixing the strained rubber.

If a section is cut from this same slab across a line of overflow, and this section is examined under a not very powerful microscope, a relatively thin, strongly double-refractive area will be seen in the overflow (Figure 1, C), which continues for half the thickness of the specimen. The region of high molecular orientation, to which the double-refraction corresponds, has its limits sharply defined under these conditions.

The rubber which remains in the injection channels, in the case of injection (transfer) molding, is in a condition similar to that just examined. Figure 2 gives the appearance of a section of rubber vulcanized in the channel, with Nicols still crossed. A very strong double refraction is noted at the center. By drawing the rubber cylinder by hand along its axis, it is often possible to obtain internal breakdown without its spreading to the surrounding area—that is, the elongation to break of the fibers internally oriented is very easily exceeded, and this, like that which occurs in the case of strongly calendered slabs vulcanized at a low temperature, is decidedly reduced in the direction of orientation⁹.

The examination can be easily extended to a completed article produced by injection (transfer) molding, if this has a constant thickness of a few millimeters; it is then possible to follow the directions of flow and their regularities

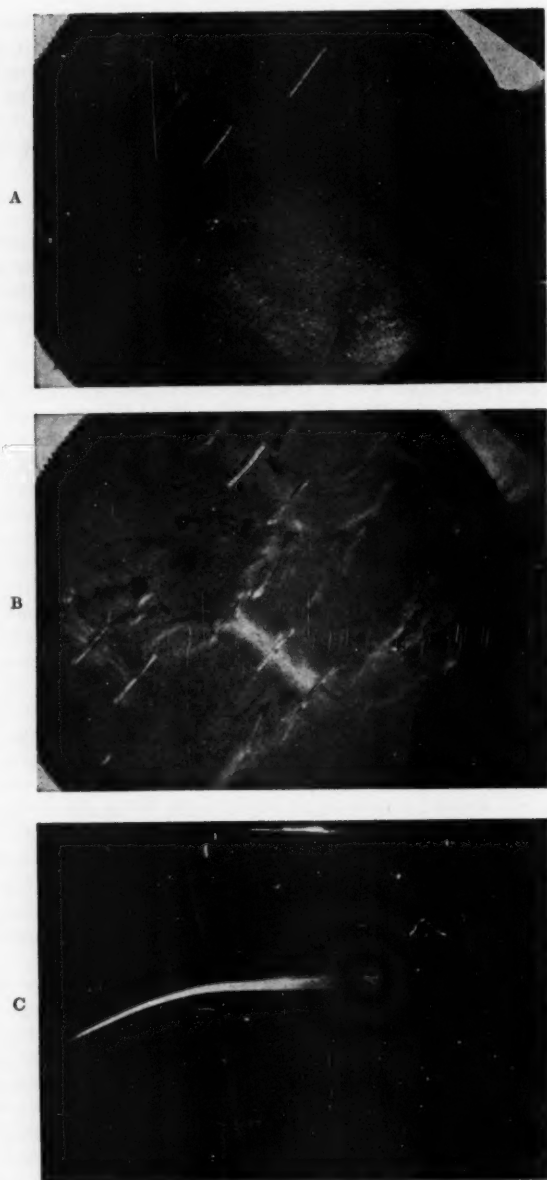


FIG. 1.—Part of slab of transparent Compound A, showing brilliant traces of openings.

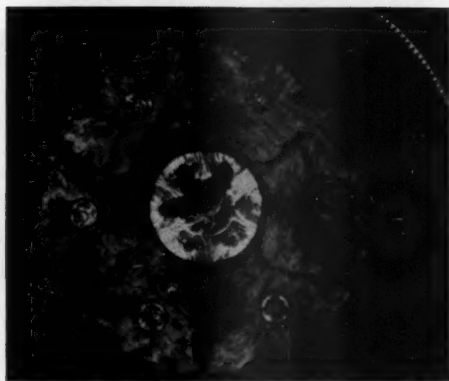
- A. Vulcanized for 60 minutes at 120° C. Crossed polaroids. Scale 1 to 3
B. Vulcanized for 10 minutes at 151° C
C. Section 50 μ thick of slab cut across line of overflow. Crossed Nicols. 10 \times



Fig. 2.—Section of overflow produced in transfer molding. Compound A, 50 μ thick. Crossed Nicols. 5 \times



A



B

Fig. 3.—Injection-molded articles of Compound A.

A. Scorched for 3 minutes at 110°C. Vulcanized for 40 minutes at 127°C. Crossed polaroids. Scale 1 go 2

B. Scorching time 7 minutes at 100°C



FIG. 4.—Sections from injection-molded articles with progressively increasing scorching time. 2-mm. sections. Crossed polaroids. 2×

(Figure 3, A), whether the symmetry of the mold is respected or not. Above all, it can be seen whether scorching has prematurely taken place in the compound, which considerably alters the appearance of the product under polarized light (Figure 3, B), even when the molding appears to the naked eye to be perfectly regular.

An almost complete absence of double refraction can be obtained with the same compound molded normally in the same mold, or a more plastic compound molded at a lower temperature, or again by using a compound much less likely to scorch (Formula D instead of A).

If the dimensions of the object are irregular or too big, large sections having a constant thickness of 1 or 2 mm. can be taken from the article molded from a transparent mix; these sections can be examined between polaroids. As the scorching of the compound to be molded increases, the double refractions in the section of the mold product become more uneven, as can be seen in Figure 4, illustrating three different degrees of scorching, at the last of which injection molding becomes impossible.

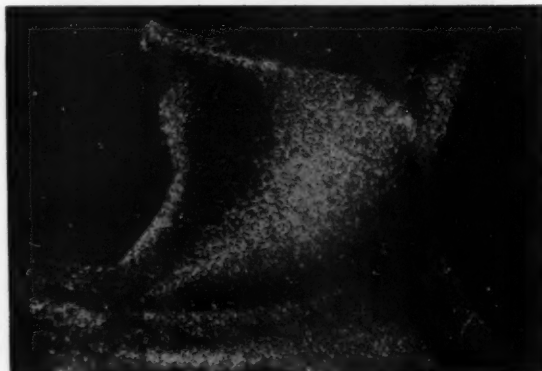


FIG. 5.—Section of small injection-molded specimen. Compound C with 15% talc. Crossed Nicols. 12×

The orientation of the acicular or flattened type particles of a compounding ingredient is very easily ascertained by using Formula C; Figure 5 shows the section of a small injection molded specimen containing 15 per cent of talc, with crossed Nicols. In normal light the section seems to be perfectly uniform, whereas under polarized light the distribution into areas of different orientation is evident. The behavior of the individual particles can be examined under normal light at a higher magnification, but obviously this is more complicated than examining the whole section at once under polarized light.

The examination becomes less obvious with a higher concentration of the ingredients or when the particles are finer, but there is reason to suppose that the marked orientation of the particles now observed is maintained.

An interesting examination of the orientation of the talc particles can be made by observing the section of a calendered sheet made of Compound C, with 1 per cent of talc. The particles have a tendency to be oriented in the direction of calendering, but this tendency is not always complete or uniform throughout the thickness of the sheet. Figure 6 shows, side by side, the same section of this



Fig. 6.—Section of calendered sheet photographed twice with different orientation of Nicols.
Compound C with 1% talc. Crossed Nicols. 10×

sheet photographed between crossed Nicols, with the principal directions differently oriented in each of the two cases.

The majority of the brilliant particles which appear in one photograph are dark in the other, indicating a good collective orientation in the direction of calendering; but the particles in a central band are partially obscured in the first photograph, and decidedly brilliant in the second, from which it can be concluded that they are differently oriented.

This lack of uniformity in orientation of elongated particles in the calendered sheet has repeatedly been observed; the general orientation of the filler particles caused by calendering has in the meantime been recorded.

A much more detailed structure of the anisotropy produced by movement during vulcanization or processing appears when Formulas B and E are used with a slight addition of active black, but not enough to make sections 30 to 50 microns realized with the microtome definitely opaque. By making a slab similar to that of Figure 1, *A* and *B*, with such a compound, and cutting a section across a line of overflow (Figure 7), a much more complicated structure

results instead of the thin luminous brush seen in Figure 1, *C*; the structure now completely covers the entire area of the microtome section. Still more revealing is a section taken from the overflow beyond the opening (Figure 8). It is not necessary to confirm that in normal light the sections are completely uniform, apart from some parallel marks of the microtome blade.

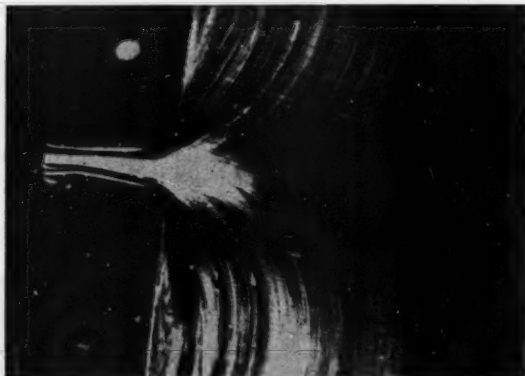


FIG. 7.—Section of slab cut across line of overflow.
Like Figure 1, *C*, but with Compound B, 1% carbon black.
Section 30μ thick. Partly crossed Nicols. $10\times$

The small injection-molded specimen which, when made with Compound C (Figure 5), indicated the oriented particles of talc shows a finer and more detailed structure when made with Compound B (Figure 9), giving a better idea of the complex movements of the injected mass.

When tension stress-strain tests are carried out on 44.5/52.5-mm. Schopper rings, they are cut from disks 57 mm. in diameter. The overflow of such a vulcanized disk, made with Compound B or E, shows in section a strong double refraction, which in fact originated these examinations (Figure 10). The flow



FIG. 8.—Section of overflow beyond opening.
Compound B, 30μ thick. Partly crossed Nicols. $10\times$

of rubber toward the overflow is, however, easily seen in the peripheral regions of the disk (Figure 11, *A*). It also spreads inside the ring, which is punched with double circular knives and has not a very square outline; a section is shown in Figure 11, *B*. The tension stress-strain test is therefore made on specimens

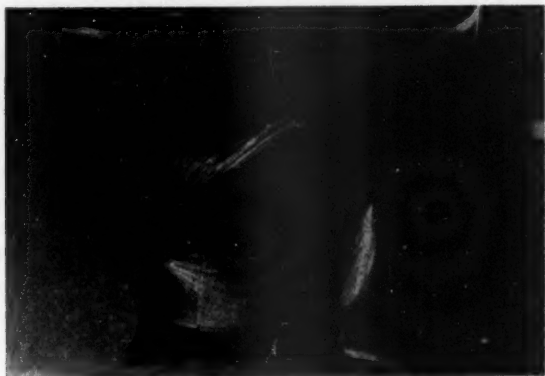


FIG. 9.—Section of small injection-molded specimen.

Compound B with 1% carbon black. Section 30μ thick. Partly crossed Nicols. $12\times$

which are clearly anisotropic, in the case of the compounds examined; but the optical criterion is perhaps excessively sensitive.

All blacks give rise to this phenomenon, although to a lesser degree when the diameter of the particles is greater—for example, lampblack is less suitable than



FIG. 10.—Section of overflow of disk for Schopper rings.

Compound E. Partly crossed Nicols. $45\times$

active or semiaactive blacks. Red iron oxide, however, also behaves in the same way, with some dichroitic effect. When dealing with other white ingredients, the actual double refraction of the particles, or the repeated refractions of light, disturb the phenomenon.

The characteristic anisotropy visible in mixings containing a slight percentage of black is not confined to natural rubber mixes. The behavior of synthetic elastomers, such as chloroprene, styrene, nitrile, and polyisobutylene rubbers, is similar.

It is difficult to explain why such a small percentage of a fine pigment reveals a double refraction even when there are very slight movements. It can be supposed that the relaxation of the deformed rubber molecules is slower when very fine particles are dispersed between them, or that there is an orientation of the chains on which the structure of a carbon black depends. Even if the second hypothesis is true, the practical and theoretical interest of the examination is not lessened, and it is only to be regretted that an equally simple examination of compounds having a high percentage of carbon black, where the effect should be even greater, is not possible.

The introduction of talc has made it possible to note a lack of uniformity in the orientation of the particles of calendered sheets, but if 1 per cent of carbon black is added, a much finer and more complex structure, predominantly strati-

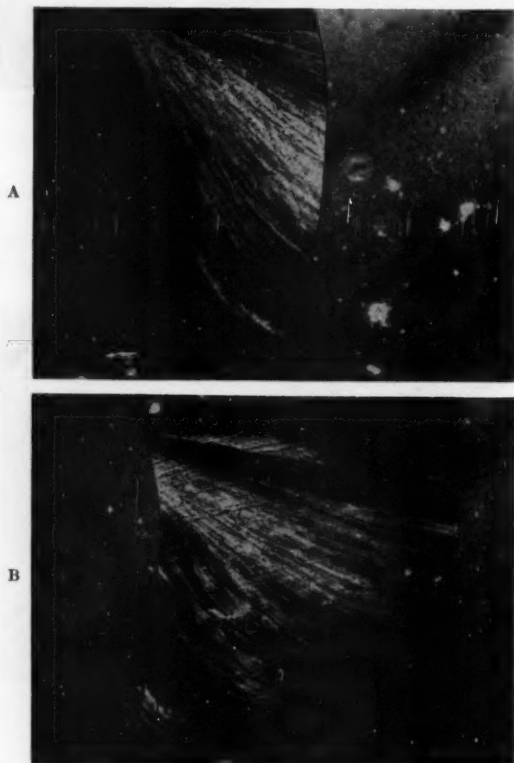


FIG. 11.—Section of Schopper ring disk.

Compound E. Partly crossed Nicols.

A. Peripheral region of disk

B. Section of ring for stress-strain test cut from disk



FIG. 12.—Section of calendered sheet.
Compound B with 1% carbon black. Partly crossed Nicols. 15X

fied, as in Figure 12, can be observed in calendered vulcanized sheets. The flows of rubber along the surface of the two cylinders (perhaps at different temperatures), with a partial return of material when they join together to form the sheet, cause a complex distribution of shear rates leaving clear traces when observed under polarized light. We do not yet know, then, even in the simple case of calendered sheets, when it will be possible to find, not an isotropic, but a uniformly anisotropic material.

SUMMARY

The anisotropic behavior of vulcanizates is revealed by differences in modulus, breaking load, and tear, swelling in solvents, and electrical properties, according to the direction of test. Anisotropy is attributed both to a state of tension in the rubber phase alone and to a preferential orientation of the elongated particles of certain fillers. It has recently been recognized that anisotropy due to movement of the stock in the mold during the first phase of vulcanization is of very great importance.

By submitting overflow slabs, sheets, and test-pieces to examination under transmitted polarized light, it is relatively easy to obtain optical evidence of the presence of anisotropy caused by movements during molding operations. The localization of the movements may make it desirable to examine with a microscope at low magnification microtome sections of the vulcanizates 50 microns thick. A transparent gum compound can be used, but more details can be seen if 1 per cent of carbon black is added. The transparent compound may be used under polarized light for the direct examination of samples a few millimeters thick or of sections of equal thickness taken from products of different dimensions.

In injection-molded products, it is possible to tell from variations of double refraction when molding conditions favor scorching before the rubber has come to rest. If talc or some other ingredient with elongated strong double-refractive particles is introduced into the transparent compound, it is possible to observe the orientation of the particles caused by the processing or molding flow. In a calendered sheet, the talc particles lie almost parallel to each other, but toward the center of the sheet the orientation may be less marked or may occur along slightly different directions. In injection molding the talc clearly reveals flow direction and anisotropy. Under optical observation, in restricted areas,

the difficulty of obtaining entirely isotropic rubber products is confirmed. Almost pure-gum compounds have been examined, but the anisotropy found will probably assume even greater importance in loaded mixings, especially those loaded with carbon black.

ACKNOWLEDGMENT

Grateful acknowledgment is made to Luigi Emanuelli, managing director of the Pirelli Co., for permission to publish this paper.

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VULCANIZATION OF SYNTHETIC RUBBERS*

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Although for a century since the discovery of the vulcanization of rubber by sulfur many investigators have worked in this field, the problem of vulcanization can still not be considered to be well understood, either from the theoretical or the practical point of view. The basis of the most widely accepted theory of vulcanization of rubber is the concept of bridges, according to which the vulcanizing agent, sulfur, unites the macromolecules of rubber into spatial chains by primary valences.

The concept that such spatial structures are formed during the vulcanization process explains well the decrease in the degree of saturation of the rubber and the changes in its physical properties, *e.g.*, decreases in solubility and plastic flow, and considerable increases in strength, modulus, and resilience. A number of experimentally established facts, however, can never be reconciled with the bridge theory of vulcanization, especially when the vulcanization of synthetic rubbers is investigated. As a consequence of this, a number of investigators¹ in this country have pointed out the shortcomings of the bridge theory and the necessity of finding a better explanation of the physico-chemical and colloidal reactions which take place during the vulcanization of rubber.

More recently Dogadkin and his associates² have shown that even when an accelerator is added, which leads to an increase of the bridge sulfur content of the vulcanizate, the total amount remains insignificant, *e.g.*, in the case of natural rubber it amounts to only 7-10 per cent and, in the case of synthetic rubber, to 2-6 per cent of the total bound sulfur.

Hence, 90-98 per cent of the bound sulfur does not play any part in the supposed formation of bridges. Since rubber can be vulcanized with a very small percentage of sulfur, *i.e.*, about 1-2 per cent by weight of the rubber, the proportion of bridge sulfur is insignificant.

This indicates the great importance in the vulcanization process of sulfur, which reacts intramolecularly with the rubber, with union at the double bonds and formation of polar groups. It is well known that the macromolecules of unvulcanized natural rubber are united to each other by van der Waals forces. These forces are small, and for this reason natural rubber is not strong and is not very thermoplastic. In plastics which have strong constant dipoles due to introduction into the polar groups of oxygen, nitrogen, and chlorine (in most cases), the polarity increases greatly the attraction between the polymeric chains. All plastics can be arranged in a series, at one extreme of which is unvulcanized rubber with hydrocarbon macromolecules, united by weak van der Waals forces, and at the other extreme, cellulose with stronger polar intermolecular bonds, with consequent toughness, hardness, and strength of the structure.

Work by Kargin, Aleksandrov, Dogadkin, Kobeko, Zhorkov, and others on the properties of plastics under different conditions has given valuable results

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Reports of the Academy of Sciences (USSR)*, Vol. 73, No. 1, pages 129-132 (1950).

which permit us to judge the molecular structure of high molecular compounds from the changes in their mechanical properties.

It should be noted that the properties of certain plastics change particularly sharply with increase in temperature, since the thermal activation weakens the attraction of the constant dipoles. Weakening of the bonds results in a decrease of the periods of relaxation, a decrease of modulus, especially at slow rates of deformation, and a decrease of strength. All these properties are an indication of structure formation in the reaction of the polar groups, and not of the formation of bridges which connect the chains by primary valences.

A study of the mechanical properties of synthetic-rubber vulcanizates at different temperatures makes it possible to trace the change of the intermolecular reactions which depend on the type of rubber, on the degree of vulcanization, and on the proportions of the vulcanizing agents, and to establish the importance of the different types of bonds in the formation of spatial structures.

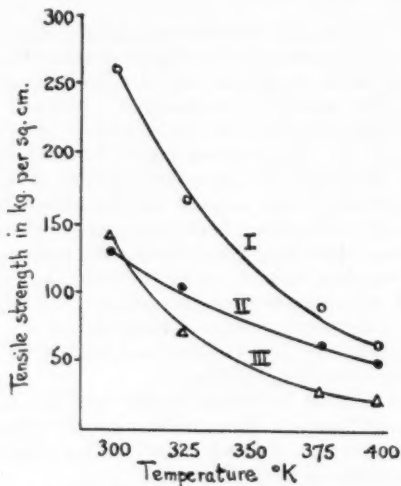


FIG. 1.—Change of tensile strength of vulcanizates with rise of temperature. I. Butadiene-styrene copolymer. II. Sodium-butadiene rubber. III. Polychloroprene.

Pisarenko³ showed that, with increase in the temperature of vulcanization of synthetic rubbers up to 190–200° C, the part played by ordinary vulcanizing agents decreases progressively, and the vulcanizates obtained are less stable. This indicates the increasingly important part played by the intermolecular bonds of the chains, not because of the primary valences, but as a consequence of the reaction of the polar groups and the hydrogen bonds which may be formed by the introduction by milling of a large proportion of oxygen. Moreover, even groups like CH_2 , $\text{CH}:\text{CH}$, and $\text{CH}:\text{CCH}_3$, as Mark⁴ has shown, govern the energy of attraction on a chain length up to 5 Å, with coordination number 4 up to 1000–1300 calories per mole, which for a macromolecule gives quantities strictly proportional to the strength of the chemical bonds.

In accord with the results obtained in the present work at elevated temperatures, vulcanizates of synthetic rubbers show considerably lower moduli of elasticity, tensile strength, and even maximum elongation.

It should be noted that the lowering of these properties depends on the type of rubber from which the vulcanizate is prepared (see Figure 1).

Our study of the vulcanization process of the rubber particles in synthetic and natural latexes showed that in cases where it is impossible to assume the formation of sulfur bridges in the macromolecules of rubber from the individual particles of latex, the films all showed the effect of vulcanization, that is, increased strength and elasticity, and lower solubility or swelling in solvents. In this case vulcanization can be explained by an increase of the polarity of the rubber molecule with the intramolecular addition of sulfur or other vulcanizing agent and by the increase in the intermolecular forces which depend on the polar groups.

According to the bridge theory, it would be natural to expect increased strength of the vulcanizates with increase in the percentage of chemically bound bridge sulfur as a consequence of the union of the sulfur with the molecular chains of rubber into a spatial network by primary valences. However, no increase of strength of sodium-butadiene rubber, even with the introduction of a relatively great proportion of sulfur (up to 12 per cent based on the rubber) was observed.

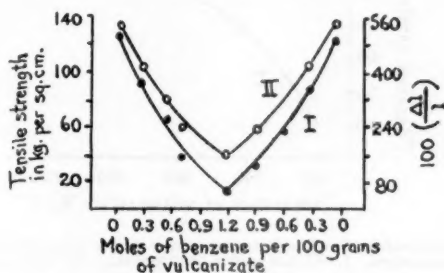


Fig. 2.—Change of tensile strength and change of elongation at rupture as functions of the consumption and loss of benzene vapor.

The kinetics of the change in properties of vulcanizates on swelling in vapors of polar and nonpolar solvents also makes it possible to determine the character of the intermolecular bonds which are formed between the chains in the vulcanization process.

It can be assumed that, with the absorption of the solvent by the polymer during swelling, most of the bonds of the spatial chains which are not of a strictly chemical nature are broken as a result of rupture of the bonds of the chains, with resulting decrease of strength and of the time of relaxation.

Our experiments on the kinetics of swelling of vulcanized synthetic rubbers in the vapor phase of polar and nonpolar solvents have shown that the decrease of strength and elasticity of rubbers is almost proportional to the amount of solvent absorbed, and have proved also that this decrease is temporary, since, when the solvents are removed, the original properties are almost wholly restored (see Figure 2).

The phenomenon observed is analogous to the change in properties during swelling of nonvulcanizing plastics which do not possess double bonds, *e.g.*, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, and similar types, whose intermolecular bonds are formed by polar groups. In a study of the structural action of fillers on sodium-butadiene rubber, we observed that the

degree of structure formation brought about by a filler is proportional to the activity of the filler. Thus, the most active filler, channel carbon black, when in high proportion in rubber increases the insolubility of the rubber, whereas the unsaturation of the rubber does not change.

A study of the elastic-viscous properties of the system by a method analogous to that employed in our laboratory⁵ showed that, with increase of activity of the filler, the modulus of elasticity E_1 in most cases increases; in addition both viscosities, *viz.*, the intrinsic or relaxation viscosity η and the viscosity of the elastic after-effect η_2 , and also the elasticity of the system increase.

By thermal treatment of rubber-carbon black mixtures at high temperatures (200–225° C), normal types of vulcanizate are obtained. The unsaturation of rubber in this case decreases by 5–8 per cent; nevertheless, the vulcanizates, on the addition of certain peptizing agents, can be mechanically destroyed and again vulcanized.

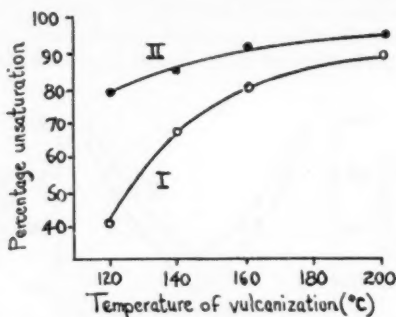


Fig. 3.—Change of unsaturation of sodium-butadiene rubber during vulcanization as a function of the temperature of vulcanization. I. Without carbon black present. II. With carbon black present.

In the vulcanization of sodium-butadiene rubber in the presence of sulfur, the peculiar structural activity of carbon black is again evident, especially when the temperature is raised to 200° C. Figure 3 shows the change of unsaturation of rubber-carbon black mixtures and rubber mixtures containing no carbon black which were subjected to the same heat treatment. A decreasing rate of fall of unsaturation in the presence of carbon black, and less mechanical destruction of the structure of vulcanizates containing carbon black, when the reversibility of the process is determined, leads to the conclusion that there is a blocking of the carbon of the double bonds of the rubber during structure formation by fillers.

Thus, the effect of vulcanization may be achieved as readily with destroyed "strong" intermolecular bonds of the "bridge sulfur" type as with "elastic" bonds, and to a considerable degree with reversible polar bonds.

The introduction into the vulcanizate of peptizing agents and substances which solvate the polar groups, especially in the absence of oxygen, makes a reversible process possible.

ACKNOWLEDGMENT

The authors express their gratitude to their fellow member of the Academy of Sciences of the USSR, V. A. Kargin, for his valuable advice in connection with this work.

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MOLECULAR STRUCTURE OF STYRENE-BUTADIENE COPOLYMERS

DYNAMIC MECHANICAL MEASUREMENTS*

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It is well known that the physical properties of a synthetic rubber are markedly affected by changes in the polymerization conditions and ingredients making up the polymerization recipe. These differences in properties in turn can only be the reflection of differences in the molecular structure of the materials. This is illustrated, for instance, by the difference between cold rubber and regular GR-S rubber¹. An even more striking illustration was reported by Schildknecht² with polyvinyl isobutyl ethers, where, by changing the polymerization conditions, the polymer can be made to have either the properties of a rubber or of a rigid solid. At various times during the last few years, differences have been found in materials of the same overall composition at this laboratory. In this preliminary work some of these structural changes have been investigated in more detail.

EXPERIMENTAL METHODS

A series of styrene-butadiene copolymers prepared under a variety of conditions and composition ratios was used for this investigation. These materials were for the most part prepared by emulsion polymerization, using well known techniques. They have a styrene-to-butadiene ratio greater than that found in GR-S. The composition of the copolymers and some of the polymerization variables, where known, are given in Table I. The styrene content was determined from the refractive index³. The extension of the refractometric method to determine the styrene content up to 75 per cent styrene in a butadiene-styrene copolymer was developed at Monsanto's Central Research Laboratory.

The study of the interrelationships between polymerization conditions, molecular structure, and physical properties is still in its infancy. The many properties of a rubber are a complex combination of both the intermolecular and intramolecular factors making up the structure of the bulk material. Any single experimental technique can be sensitive to only part of these structural factors, so several types of experiments must be carried out to characterize a given material. For this investigation three physical methods were chosen which tend to be characteristic of widely different aspects of molecular structure. These experimental methods are dynamic mechanical tests, swelling measurements, and infrared spectroscopy.

Infrared spectroscopy can be used to determine the relative amounts of *cis-trans* isomerism and 1,2-addition or 1,4-addition in such polymers as several investigators have shown⁴. This is an especially powerful method of determin-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 341-345, February 1951. This paper was presented before the Division of Rubber Chemistry at its International Meeting in Cleveland, October 11-13, 1950.

TABLE I
 COMPOSITION AND PROPERTIES OF COPOLYMERS

Copolymer ^a	Styrene (%)		Catalyst ^b (%)	Regulator ^c (%)	Conversion (%)	Gel (%)	Swelling index	[η] of sol fraction	Temp. of maximum damping (° C)
	Charged	Determined							
1	60	60.0	0.3, A	0.2, M	93.6	66.6	65.8	0.639	+7
2	60	57.5	0.3, A	0.8, M	96.3	0	—	0.612	+4
3	60	54.2	0.3, A	0.2, M	71.4	0.5-1.0	140	1.53-1.62	-5
4	45	44.5	0.5, A	0.2, M	93.5	10.4	112	1.51	—
5	45	44.5	0.5, A	0.8, M	95.9	21.6	124	1.255	—
6	60	55.8	0.15, B	0.6, N	91.2	8.2	150	1.774	—
7	60	—	0.15, B	0.2, N	—	52.3	34.8	1.38	—
8	60	57.8	0.3, B	1.0, O	92.2	1	42.5	0.943	—
9	60	58.0	0.3, A	0.5, O	—	87.4	21.65	0.181	—
10	60	59.5	0.3, A	0.5, O	88.4	90.24	23.8	0.150	+5
11	60	—	0.3, A	1.0, O	92.2	86.3	25.6	0.653	—
12	60	—	0.3, A	0.8, M	94.8	49.1	54.3	0.708	—
13	60	—	—	—	—	78.5	27.4	0.328	+10
14	—	43.5	—	—	—	84.1	17.3	0.265	—
15	50	44.0	—	—	—	80.9	25.4	0.5725	-12
16	85	—	—	Yes	—	—	—	—	+79
17	85	—	—	No	—	—	—	—	—

^a Copolymers 1-12 were polymerized at 50° C; copolymers 13-17 are commercially available.

^b A = Cumene hydroperoxide; B = potassium persulfate.

^c M = mixed tertiary thiol; N = dodecanethiol (kerosene); O = tertiary C₁₆ thiol.

ing the atomic groups and their configuration within the individual molecules.

Swelling measurements in solvents are useful for determining the percentage of material that has been cross-linked to give a network structure and the closeness of the cross-links in the network.

Dynamic mechanical tests in which an elastic modulus and damping are measured over a temperature range, are useful for determining the response of various structural units in a substance to an applied mechanical force. By this method transitions in polymers and an indication of the degree of molecular heterogeneity can be established. The use of dynamic mechanical methods for determining structure is quite new and is only beginning to be explored⁵. There is still much to be learned in this field, but in metallurgical fields especially such methods have been of great value⁶.

RESULTS

Swelling measurements.—Swelling measurements were made on these rubbers in benzene. The measurements give three quantities that are characteristic of a material: the ratio of sol to gel, the swelling index of the gel portion, and the intrinsic viscosity of the soluble portion⁷. The experimental techniques used in these measurements have been described in the report of the Rubber Reserve Company⁸. Most of the experiments were carried out at 25° C (Table I).

The results are in general agreement with the findings of other investigators. High conversions in the polymerization stage tend to give rubbers in which most of the material is a gel. Polymerization regulators such as thiols decrease the amount of material in the gel phase and usually decrease the intrinsic viscosity of the sol fraction, but not in all cases. If most of the material is in the gel phase, it is possible for the intrinsic viscosity of the soluble portion to actually increase as the amount of regulator is increased. In general, rubbers having a low gel content also have a high swelling index⁹. If the cross-linking reactions have occurred only to the extent of giving a small amount of gel, then this gel, itself will have a low concentration of cross-linking points, so it is capable of swelling to a very large volume. This general trend, however, is quite depend-

ent on the catalyst, regulator, and other polymerization conditions, so there is not a unique value of the swelling index for a given gel content.

Much of the same type of information can be obtained from a creep test as from swelling measurements—for instance, a rubber that is mostly in the form of a gel deforms when a constant force is first applied, but the deformation does not increase much with time because the network structure prevents viscous flow. This is illustrated by curves 1 and 3 of Figure 1. Here compliance rather than deformation is plotted, but for a constant load or stress the compli-

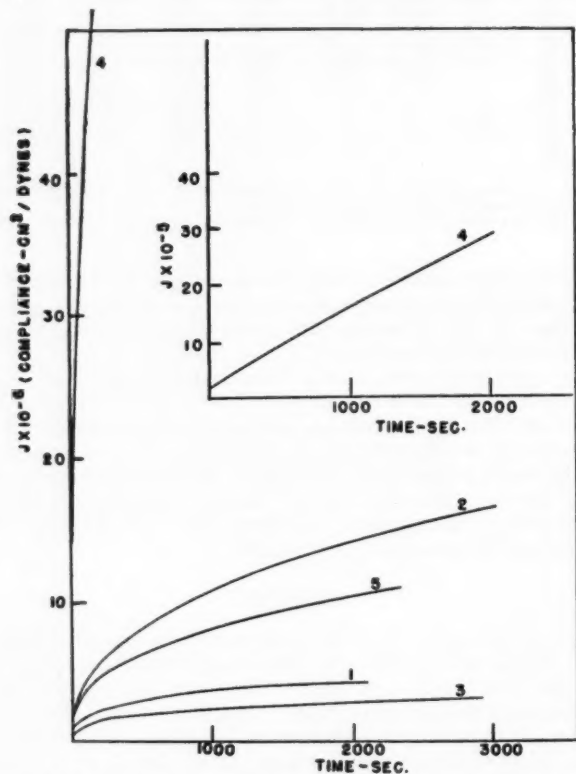


FIG. 1.—Creep of styrene-butadiene copolymers measured 50°C above transition temperature. Curve 1 = 13; curve 2 = 3; curve 3 = 15; curve 4 = 2; curve 5 = 1 (Table I).

ance is proportional to the deformation. A low molecular weight, noncross-linked rubber gives a creep curve in which the deformation increases linearly with time because viscous flow can occur. This is illustrated by curve 4 of Figure 1. High molecular weight, noncross-linked rubbers or rubbers in which there is only a moderate amount of gel give creep curves between these extremes. Such rubbers are shown in curves 2 and 5 of Figure 1. These creep curves were obtained with a parallel plate plastometer¹⁰ at a temperature of 50°C above the transition temperature of each rubber. The method of obtaining

this transition temperature will be discussed later. As Mooney has pointed out¹¹, there are certain advantages in making comparative tests at equal temperatures above the transition temperatures rather than at a single temperature for all the rubbers.

Infrared spectra.—Infrared spectra of these copolymers have been determined from 2.5μ to 16μ , using a Perkin-Elmer Model 12B spectrometer. The most interesting differences appeared in the neighborhood of 11μ . The initial work was done on thin films, but later solutions of the rubbers in carbon disulfide

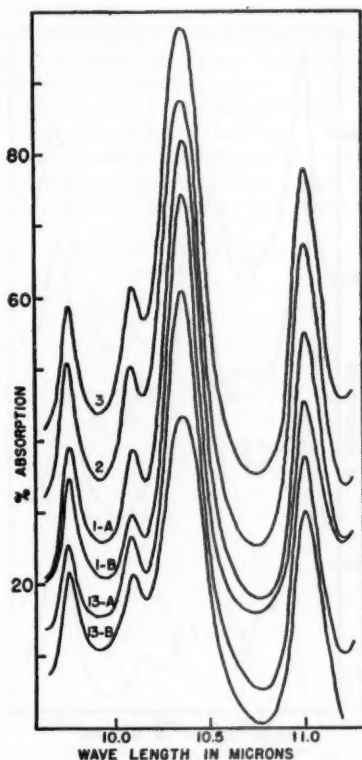


Fig. 2.—Infrared spectra of styrene-butadiene rubbers (Table I). A = sol fraction; B = gel fraction; each curve displaced about 5%; bottom one in proper position.

were found to be more satisfactory. Some of the infrared absorption curves are shown in Figures 2 and 3. In rubbers 1, 13, and 17 both the gel and sol fractions were studied. For rubber 1, the ratio of styrene to butadiene was the same in both the sol and gel fractions; however, there was less 1,2- and *trans* 1,4-addition in the gel portion. This means that relatively more of the butadiene was in the *cis* 1,4-configuration⁴. The gel fraction of rubber 13 contained a considerably higher ratio of styrene-to-butadiene than the sol portion. It appeared that the reverse was true for rubber 17, but it was impossible to make

an accurate determination to check this point with certainty. The absorption spectrum of rubber 10 showed that there were considerable amounts of $\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \text{O}$ and $\begin{array}{c} \diagdown \\ \text{C} \\ \diagup \end{array} \text{O}$ linkages in the material. Figure 3 shows part of the absorption curves of rubbers 16 and 17, which had the same styrene-to-butadiene ratio but which were quite different in physical properties because of differences in

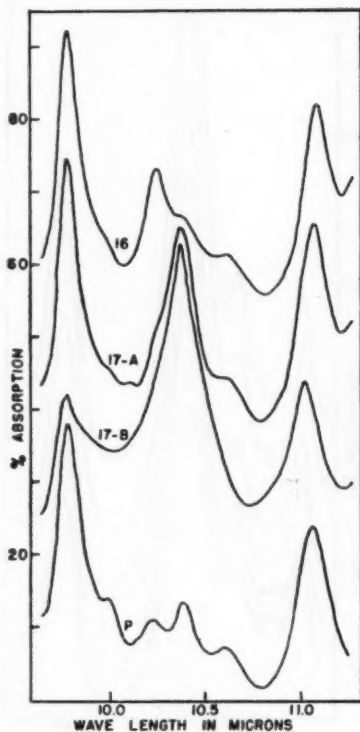


FIG. 3.—Infrared spectra of styrene-butadiene copolymers (Table I). A = sol fraction; B = gel fraction; P = polystyrene; each curve displaced about 15%; bottom one in proper position.

polymerization conditions, such as regulator concentration. One of the differences in absorption spectra was a shift in the 11.0μ band to 11.1μ for copolymer 16 and the sol portion of copolymer 17. Vinyl compounds (1,2-addition) are characterized by an absorption band at 11μ , whereas polystyrene has an absorption band at about 11.1μ . The observed shifts might be explained by the polystyrene band overlapping the vinyl band in a product which has only a small amount of 1,2-addition. Data on the percentage of 1,2- and *trans* 1,4-addition, based on the amount of butadiene in the rubbers, are presented in Table II.

TABLE II

AMOUNT OF 1,2-ADDITION AND *trans* 1,4-ADDITION OF VARIOUS COPOLYMERS

Copolymer no.	Styrene/ butadiene	1,2-Addition (%)	<i>Trans</i> 1,4-Addition (%)
1 (sol)	59.2/40.8	14.5	48
1 (gel)	59.2/40.8	10.0	37
2	57.5/42.5	13	28
3	54/68	12.3	37.8
13 (sol)	45/55	8	24.8
13 (gel)	63/37	7.3	21

Dynamic mechanical properties.—A recording dynamic mechanical tester based on the principle of a torsion pendulum was used to determine the shear modulus and damping over a temperature range¹². In this apparatus the plastic or rubber specimen is attached to a moment-of-inertia disk and is allowed to twist and untwist as it carries out free vibrations. The oscillatory motion of the specimen is converted into electrical potentials by means of a linear variable differential transformer on a torque measuring device attached to one of the specimen clamps. The electrical potentials are eventually recorded on the

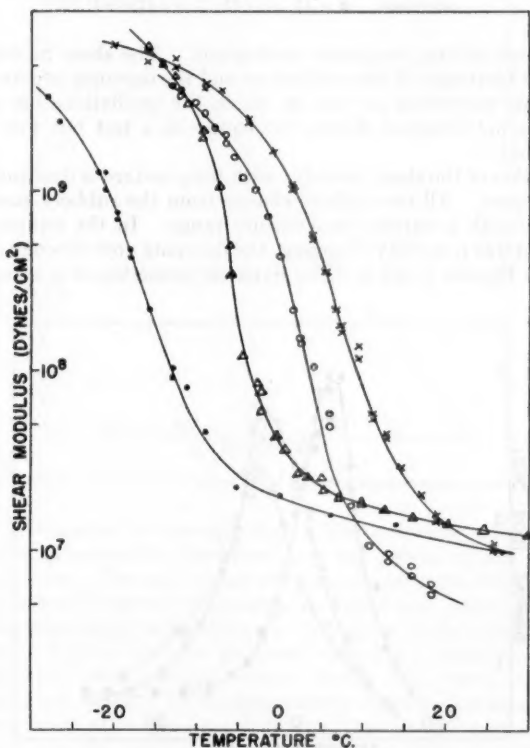


FIG. 4.—Dynamic shear modulus of styrene-butadiene copolymers.
● = 15; × = 13; ○ = 2; Δ = 3 (Table I).

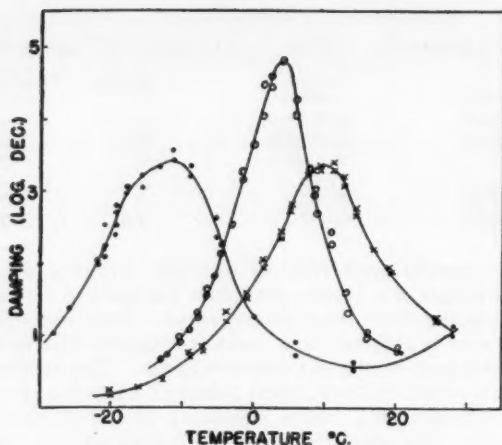


Fig. 5.—Mechanical damping (logarithmic decrement) of styrene-butadiene copolymers. ● = 15; X = 13; ○ = 2 (Table I).

chart of a direct writing magnetic oscillograph. The shear modulus is calculated from the frequency of the oscillations and the damping is determined from the logarithmic decrement or rate at which the oscillations die down. The frequency was not constant during the course of a test but was roughly 0.2 cycle per second.

The variation of the shear modulus with temperature is illustrated in Figure 4 for four rubbers. All the rubbers change from the rubbery state to a hard rigid state through a narrow temperature range. In the temperature range where the modulus is rapidly changing, the damping goes through a maximum, as is shown in Figures 5 and 6. The dynamic properties of a material can, for

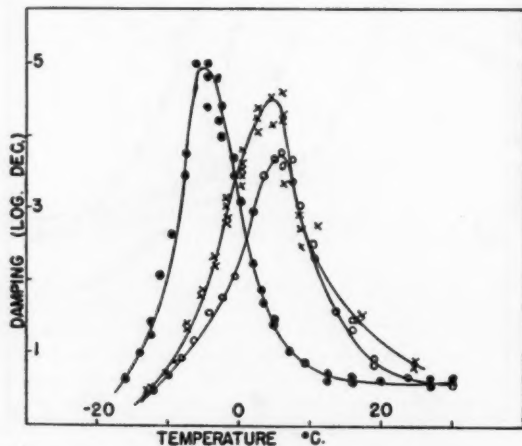


Fig. 6.—Mechanical damping (logarithmic decrement) of styrene-butadiene copolymers. ● = 3; X = 1; ○ = 10 (Table I).

the most part, be characterized by the temperature at which damping is a maximum and by the width of the damping peak. The temperature of maximum damping has been shown for various types of high polymeric materials to occur in the neighborhood of the second-order transition temperature. In general, at low frequencies the temperature of maximum damping is a few degrees higher than the second-order transition as determined by volumetric measurements.

DISCUSSION

The temperature of maximum damping of various styrene-butadiene copolymers is plotted against the percentage of butadiene in the copolymer in Figure 7. The butadiene, of course, lowers the temperature of maximum

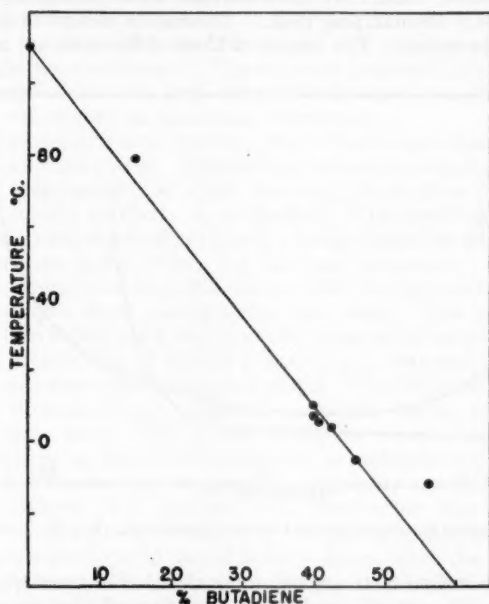


FIG. 7.—Transition temperature of styrene-butadiene copolymers.

damping as it increases in concentration. The polymers were made over a wide range of polymerization conditions, yet the points do not scatter much from a straight line. The one rubber showing the greatest deviation might be expected to behave in this way because of its broad and unsymmetrical damping peak. An interesting point about the data given in this graph is that they extrapolate to -120°C for pure polybutadiene when replotted on a volume fraction basis rather than a weight fraction basis. This would indicate that it should be possible to prepare a butadiene rubber which still retained its rubbery characteristics down to -120°C . Polybutadiene as it is normally prepared begins to harden in the neighborhood of -70°C . [Wiley¹³ lists the second-order transition of polybutadiene at -85°C and its brittle point as -66°C . It is known that the maximum in damping occurs in the same temperature

region for many polymers.] The difference between these figures, -120° and -70° C, must partly be due to the large amount of cross-linking, crystallinity, and other differences in molecular structure that occur as more and more butadiene is added to the rubber. The question immediately arises, is it proper to use this linear plot to extrapolate to a pure polybutadiene rubber? Experimental work on other copolymer systems and on plasticized polymers indicates that a plot of temperature of maximum damping against volume fraction of one of the components is linear throughout the composition range¹⁴.

The temperature of maximum damping can thus be predicted quite accurately, in general, from the composition of the copolymer. However, the width and general shape of the damping peak cannot be predicted from the overall composition of a material. Rubbers of about the same overall composition but polymerized under different conditions show marked differences in the width and shape of the damping peak. The results plotted in Figures 5 and 6 bring out this variation. The causes of these differences are not completely

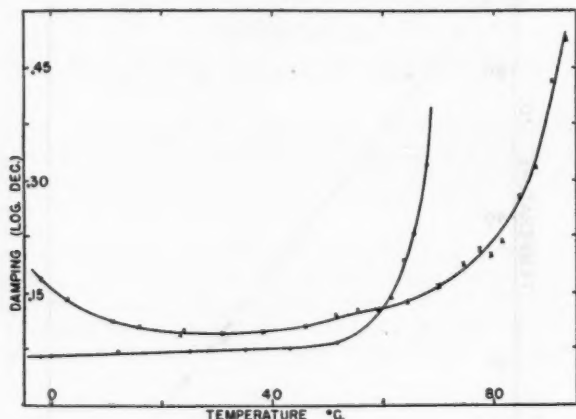


Fig. 8.—Mechanical damping of styrene-butadiene copolymers. ● = 16; X = 17 (Table I).

understood, but certain facts are becoming clear. For instance, rubbers polymerized in the presence of considerable amounts of regulators have sharper damping peaks than those prepared under the same conditions but without a regulator. It is also a general characteristic of high polymeric materials that sharp damping peaks are accompanied by correspondingly sharp changes in the modulus with temperature. This is illustrated by Figures 4 and 5, which give the damping and moduli for the same three rubbers.

The effect of polymerization regulators is illustrated further in Figure 8. Both of these materials contain about 85 per cent styrene. In Figure 8 the entire damping peak is not shown, but only a part of the low-temperature portion where the damping rapidly increases with temperature. At temperatures higher than those shown, the damping goes through the same kind of a maximum as the curves shown previously. These materials have such a high styrene content that they are not rubbers at room temperature. The regulated copolymer was hard and very brittle at 25° C. It had a small mechanical damping at room temperature and a very sharp transition region from a hard

to a rubbery material, starting at about 55° C. The unregulated copolymer, on the other hand, was hard but very flexible at room temperature and had a milky appearance. The damping was higher even at temperatures considerably below room temperature. The transition region from a rigid material to a rubbery material was broad, and ended at a temperature well above that of the regulated copolymer because some of the molecules contained more than their share of butadiene, leaving the larger portion depleted in butadiene. These differences between the two materials can largely be explained in terms of a molecular homogeneity. In the regulated copolymer it seems nearly all the molecules have about the same ratio of styrene to butadiene. However, in the unregulated copolymer some of the molecules are almost entirely made up of styrene; some contain a large amount of butadiene, and other molecules have all types of composition ratios between these extremes. In other words, the unregulated material is heterogeneous on a molecular scale. It is known that regulators tend to lower the molecular weight of a polymer and to make the molecular weight more uniform¹⁶. The evidence presented here indicates that in some instances they also can have the additional effect of making the polymer more uniform with respect to molecular composition.

These results indicate that various kinds of heterogeneities must exist in styrene-butadiene copolymers. The swelling measurements show the existence of one type of heterogeneity in which the copolymers are a mixture of a gel portion and a soluble portion. A comparison of the swelling measurements with the dynamic tests shows that there is a trend toward broad damping peaks with high gel content in the rubber, but there are exceptions. Above the temperature of maximum damping, the rubbers with low gel content and low intrinsic viscosity have shear moduli lower than usual. The modulus of non-cross-linked rubber which has a high intrinsic viscosity, however, gives a normal shear modulus comparable to that of a cross-linked material. This indicates that dynamic modulus need not depend on the degree of cross-linking. However, even in noncross-linked material, a certain degree of compositional heterogeneity must exist. Not all the molecules contain the same ratio of styrene to butadiene, so there is a distribution in molecular composition. The width of this distribution can be varied considerably by changing the polymerization conditions. For instance, this distribution can be made quite narrow by polymerizing to a low degree of conversion in the presence of a regulator¹⁶. Still another type of heterogeneity arises from the distribution in molecular weights of the soluble molecules or the distribution in molecular weight between cross-links in the gel portion of a rubber. The effects of these types of heterogeneity on the physical properties of a rubber have never been thoroughly investigated, except for molecular weight. Dynamic mechanical tests offer one method of studying these effects. There are definite indications that the width and general shape of the damping versus temperature peak are closely related to compositional heterogeneity. For instance, copolymers 2 and 3 in Table I are much more homogeneous than copolymers 15 and 17. The damping peaks for both copolymers, 15 and 17, are so broad and unsymmetrical that the transition is shifted to higher temperatures than what would be expected on the basis of their overall composition.

The differences found by dynamic tests and by swelling measurements cannot be detected by infrared spectroscopy in general. The percentage of styrene in a copolymer can be determined from the absorption spectra, and the composition, of course, usually determines the transition temperature range where the damping goes through a maximum. It is to be expected that 1,2-addition

in a copolymer would give a different transition temperature than one containing either all *cis* or *trans* 1,4-addition. However, the variations in these configurational factors were not great enough in the rubbers that were studied to be able to detect them definitely by means of shifts in the transition temperature. The differences between normal and cold GR-S give indications of what can be expected along this line, but more work is obviously needed in this field. There is an indication that low amounts of 1,2-addition give broader damping peaks than larger amounts of this type addition. Finally, no correlation was found between the swelling properties and the infrared spectra. The concentration of cross-links giving rise to gel formation is so small that any differences in absorption due to them are very difficult to detect.

SUMMARY

The dynamic shear modulus, mechanical damping, swelling properties in benzene, and infrared spectra have been determined on a series of styrene-butadiene copolymers which were prepared under a variety of polymerization conditions.

Evidence is presented which indicates it may be possible to prepare a polybutadiene rubber which retains its rubberlike properties down to -120°C . Materials of the same overall composition were often found to differ greatly in structure as determined by these experimental methods. Many of these differences can be explained in terms of various types of heterogeneity found in the copolymers. The temperature of maximum mechanical damping is primarily determined by the composition of the copolymer, whereas the width of the damping peak is related to the heterogeneity of the material.

The work reported here is part of an investigation of the differences in physical properties of polymers of like composition that occur as a result of changes in polymerization conditions.

ACKNOWLEDGMENT

Most of the copolymers described here were prepared by George Wesp and Forrest Norris.

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REFRACTOMETRIC DETERMINATION OF SECOND-ORDER TRANSITION TEMPERATURES IN POLYMERS.

V. DETERMINATION OF THE REFRACTIVE INDEXES OF ELASTOMERS AT TEMPERATURES FROM 25 TO -120°C *

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In previous papers¹ a refractometric method was described for determining second-order transition temperatures of polymers whose transitions occur between 75 and -60°C . In the present study, an Abbé refractometer was insulated and used to determine the refractive indexes of polymers down to -120°C and the transition points of natural rubber and a number of synthetic rubbers.

EXPERIMENTAL

Insulation of the refractometer.—The insulation of an Abbé refractometer requires separate coverings for the two prisms to allow opening and closing and a connecting piece to conduct the cooling medium from one jacket to the other when the prisms are closed. The description of the procedure used to insulate the refractometer for this work is described in three parts: (1) insulation of the prism jackets, (2) construction of the connecting piece, and (3) construction of the adapter for the liquid air tank. Figure 1 shows the refractometer with sample mounted before closing with the connecting piece unmounted. Figure 2 shows the prism jackets closed with the connecting piece ready to be attached. Figure 3 shows the three parts in position, and Figure 4 shows the entire assembly.

Insulation of the prism jackets.—The four nipples used as inlet, interprism connectors, and outlet for the cooling medium path are removed, machined to accommodate bushings which extend through the insulation, and can be replaced. The bushings to fit nipples a, b, and c, and the thermocouple well (e) as shown in Figure 5, are to be mounted in the connecting piece. The bushing for nipple d is put in place. A retainer screw is mounted in a hole drilled and tapped in the prism jacket. This screw reaches through the connecting piece and an attached nut serves to hold this piece in place. The swinging gate covering the upper prism opening is removed. Wooden blocks are cut to fit the necessary openings to the prism and a cardboard baffle placed between the closed prisms. These pieces extend $\frac{3}{4}$ inch beyond the surface of the prism jackets and are removed to leave openings for the light path and to separate the prisms. The insulating material (Insulag) was applied over the entire surface

* Reprinted from the *Journal of Polymer Science*, Vol. 5, No. 5, pages 609-614, October 1950. The present address of R. H. Wiley is the Department of Chemistry, University of Louisville, Louisville 8, Kentucky.

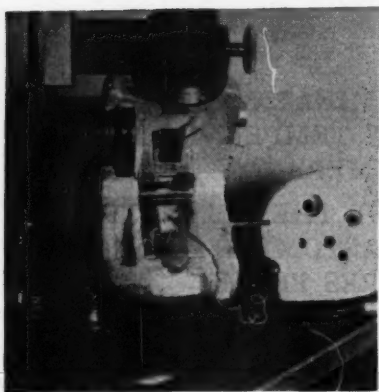


FIG. 1.

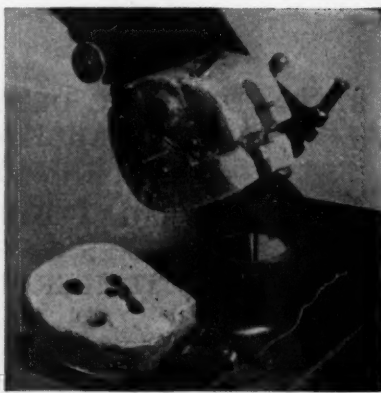


FIG. 2.

of the prism jackets, except at the hinge, as shown in the figures. The windows were cut from microscope slides and mounted with Vaseline in slits in the insulation after placing a piece of anhydrous calcium chloride in the space to be enclosed.

Connecting piece.—This unit combined the inlet bushing (nipple c), a brass connector to unit nipples a and b, the thermocouple well bushing, and the attaching screw bushing. These units are installed on the refractometer (insulated as in the previous paragraph) while on its side, and are held in place with a metal template which fits over the screw bushing and extends to each nipple. Wires were twisted around the bushings to anchor them in the insulation. The insulated face is greased with vaseline and the units covered with insulation.

Adapter.—The adapter is fitted to the top of a standard 15-liter liquid air container and serves to conduct the air stream (used as cooling medium) into

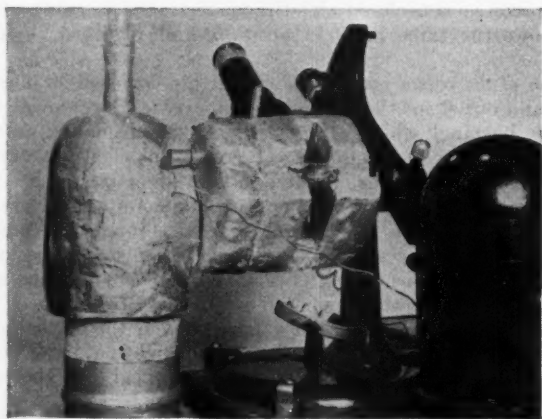


FIG. 3.

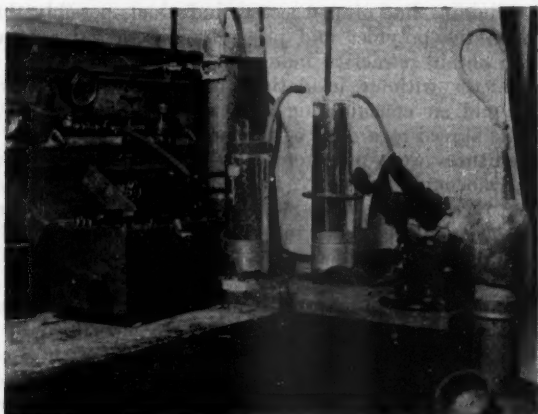


FIG. 4.

the container and out to the refractometer at its inlet bushing. It is an insulated tube with its side opening to fit and turn freely in the refractometer inlet bushing and with its vertical shaft large enough to accommodate a tube which extends down into the liquid air and is connected to the air line.

The grazing incidence technique of Arnold and Wood² was used with this refractometer by replacing the lower prism with a brass block of the same shape as the prism except for a slit opening along its face for illumination.

Operation.—The air for the cooling medium was taken from a 100-lb. pressure source and reduced and controlled with a diaphragm regulator. The air was passed through a calcium chloride drier and a dry ice precooler before introduction at the adapter. The tube extending into the liquid air container clogged up if the air was not completely dried but could be replaced quickly. By careful adjustment of the air flow, temperature control of $\pm 0.5^\circ \text{C}$ from -10 to -120°C was obtained for 10 to 20 minutes while readings of the refractive index were made. Substantially lower temperatures could be obtained by passing air through a cooling coil immersed in liquid air instead of through the liquid air container, but this method has the disadvantage of poor temperature control and excessive consumption of liquid air. At temperatures below

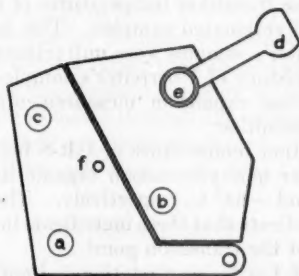


FIG. 5.—Side view of prism jackets: (a, b) interprism connections; (e) inlet; (d) outlet; (e) T. C. well; (f) retainer screw.

-120°C the dividing line often becomes indistinct, possibly through loss of contact between the polymer and prism by differential contraction. It is possible also to obtain refractive index values down to -120°C , using the Abbé refractometer without insulation, but again temperature control is difficult and liquid air consumption is increased. The refractive index and transition points agreed regardless of the method of cooling.

The temperatures were measured with a spot-welded, flattened copper-constantan thermocouple (L and N, 1938 calibration), which was placed carefully, so as not to scratch the prisms, with the sample between the prisms. The thermocouple was calibrated down to -76°C by the method of Scott⁴. Temperatures measured in the jacket thermocouple well were always lower than those between the prisms.

Refractive index readings were made most readily by the transmitted light technique, but the method of grazing incidence developed by Arnold and Wood² was also used. In the latter method the lower prism was replaced by the brass block previously described, and a pressed sample of about 0.02-inch thickness with a sharp, clear-cut edge was placed on the upper prism with the edge cut away from the observer. Both methods gave values for n_D and T_m which agreed within the experimental error of ± 0.0002 in n_D and of $\pm 2^{\circ}\text{C}$ in T_m . The method of grazing incidence has the advantage of (1) giving more distinct boundary lines, (2) avoiding possible scratching of the prisms, (3) easier cleaning of the windows, and (4) no error in the n_D value due to finite thickness of sample. However, temperatures below -110°C could not be reached by this method. The adjustment of light source to obtain a sharp dividing line is much simplified in the observation by transmitted light.

RESULTS AND DISCUSSION

The data for the polymers examined in this study are given in Table I. The second-order transition temperatures determined refractometrically agree with those obtained by the more tedious thermal expansion methods where the data are available for comparison. Several polymers not previously investigated are included in the table. The recorded brittle points are uniformly higher than the transition temperatures.

The data for the fractionated polyisobutylene show little change of transition temperature in the range of 4300 to 233,000 molecular weight. Previous data obtained by Überreiter⁵ for polyisobutylene showed a drop from -65°C for a polyisobutylene of molecular weight 200,000 to -78°C at 4000 molecular weight. Previous comparisons³ of fractionated and unfractionated polyethyl acrylates showed that the transition temperatures of fractionated samples are higher than those of unfractionated samples. This is not consistent with an assumption that Überreiter's samples were unfractionated. In the absence of additional data on the history of Überreiter's samples it is difficult to clarify this discrepancy. Thermal expansion measurements with polyisobutylenes are known to involve difficulties⁶.

Values for the transition temperature of GR-S before and after extraction of antioxidants and other nonhydrocarbon organic impurities, such as soaps and fat acids, are -67 and -65°C , respectively. These values are within the limits of accuracy, and indicate that these ingredients in the commercial polymer do not significantly affect the transition point.

Emphasis in this work has been on relative and not absolute accuracy of n_D readings. No correction was made for the change in the refractive index of the

TABLE I
TRANSITION POINT DATA FOR ELASTOMERS

Polymer	$T_m(^{\circ}\text{C})^a$	$T_m(^{\circ}\text{C})^b$	$T_B(^{\circ}\text{C})^c$	$n_D^{20}^d$	$\frac{\Delta n}{\Delta T}^e$	$\frac{\Delta n}{\Delta T}^f$	Source of sample ^g
Natural rubber ^g	-75	-73	-58	1.5188	3.6	1.0	RTA
Chloroprene ^g	-50	—	-38.5	1.5578	3.5	1.0	N
Polybutadiene ^g	-85	-88	-66	1.5190	4.0	1.8	RRC
GR-S X-387 (22% styrene) ^g	-67	—	-58	1.5325	3.9	1.1	RRC
GR-S X-387 (extracted) ^{g,h}	-65	—	—	1.5337	3.8	1.4	RRC
GR-S (25.5% styrene)	—	-61 ⁱ	—	—	—	—	—
Polybutyl acrylate	-63 ^j	—	-40	1.4634	3.7	1.1	Fi
GR-I Y-25 (3% isoprene)	-75	—	—	1.5081	3.0	0.8	EC
GR-I Y-15 (2.5% isoprene)	-79	—	—	1.5080	3.1	0.7	EC
GR-I R-2 (2% isoprene)	-80	—	—	1.5078	3.1	0.8	EC
Vistanex	-84	—	—	1.5078	2.8	1.1	EC
Polyisobutylene (M.W. 233,000)	-77	-65	50.2	1.5077	3.1	1.1	F
Polyisobutylene (M.W. 11,000)	-77	-65	50.2	1.5060	3.2	0.8	F
Polyisobutylene (M.W. 4900)	—	-78	—	—	—	—	—
Polyisobutylene (M.W. 4300)	-80.5	-78	-45	1.5018	3.0	0.9	F

^a Refractometric method.

^b Coefficient of thermal expansion. From the literature.

^c Brittle point. From the literature.

^d Above $T_m \times 1000 \pm 0.1$.

^e Below $T_m \times 1000 \pm 0.1$.

^f The authors wish to thank the various firms and individuals listed for generously providing the samples: RTA, Rubber Trade Association; N. E. I. du Pont de Nemours & Co.; RRC, Rubber Reserve Co.; Fi, C. H. Fisher (Eastern Regional Research Laboratory); EC, Enjay Company; F. P. J. Flory.

^g Samples milled for 3 minutes.

^h Extracted small strips of 0.3 g. of milled sample in three 30-cc. portions of 30% by volume solution of toluene in absolute alcohol (ethanol-toluene azeotrope) acidified with HCl at 80° C. Total extraction time 24 hours. Washed, extracted twice with acetone and dried for 12 hours at 100° C and 2 mm. Pressed the sampleⁱ.

ⁱ By heat capacity measurement.

^j Value previously reported -70° C³. This difference in T_m is due to the fact that temperature readings were previously made by a thermocouple placed in the thermometer well of the Abbé refractometer.

prism itself due to the low temperature. The change of the refractive index of glass is known only in the range of 15 to 100° C and amounts to 0.65×10^{-5} per degree⁷. It should be smaller at lower temperatures; hence, the error introduced is probably only slightly larger than the experimental error. Experiments designed to establish the absolute accuracy of the refractive index values obtained in the Abbé refractometer through the wide temperature range used for the first time in this study are being conducted. This problem is complicated by the fact that there are no primary standards available for direct calibration experiments.

ACKNOWLEDGMENT

This work was completed under Contract N7onr-284, Task Order III between the University of North Carolina and the Office of Naval Research, Navy

Department, as part of project NR-054-079. This support is gratefully acknowledged by the authors and the University.

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APPLICATION OF INFRARED ABSORPTION SPECTRA TO STUDIES OF THE OXIDATION OF SODIUM-BUTADIENE RUBBER *

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The reaction of rubber with molecular oxygen explains well the structural changes which take place in rubber during aging and during a number of important technological processes, such as plasticization and vulcanization. Furthermore, during vulcanization, in addition to its reaction with the vulcanizing agent, rubber also reacts with oxygen contained in the mixture. This may be one of the reasons for an optimum point of vulcanization.

However, it is difficult to explain the changes of physical properties of rubber by simple union of oxygen, with formation of oxygen-bearing groups. To account for the changes observed, addition of a large quantity of oxygen would be necessary, whereas actually notable changes are brought about by the absorption of only 2-3 per cent of oxygen. To explain this, it must be assumed that oxygen causes structural changes in rubber and that these changes become evident when the percentage of oxygen in the reaction products is still negligible.

In the case of sodium-butadiene rubber, as was shown by one of the authors¹, this reaction at any particular temperature causes an increase of strength and of elasticity, and a loss of solubility.

The object of the present investigation was a qualitative and limited quantitative analysis of those groups which originate during oxidation and also an examination of the structures which determine the changes of the physical and chemical properties in the reaction of rubber with molecular oxygen.

EXPERIMENTAL METHOD

The measurements were made in a range of from 2.5μ (4000 cm.^{-1}) to 11.3μ (885 cm.^{-1}) with a Hilger spectrometer.

The source of infrared radiation was a nickel-chrome coil, with a current of 9 amperes from a battery of accumulators.

The width of the slit varied for different parts of the spectrum, hence the curves are broken at the points where the slit changes. The receiver of the infrared radiation was a bismuth/silver thermopile, connected with a mirror galvanometer.

The curves of percentage transparency as a function of the wave length were constructed from the deflections of the galvanometer.

PREPARATION OF LABORATORY SPECIMENS

Sodium-butadiene rubber was investigated in the form of films $45\text{--}50\mu$ thick.

To obtain such films, a solution of rubber in benzene was poured into a frame floating on water. By removal of the solvent, a film of uniform thickness was obtained. To obtain comparable results, the changes at all stages of

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Reports of the Academy of Sciences, USSR, Physics Series*, Vol. 12, No. 5, 616-620 (1948).

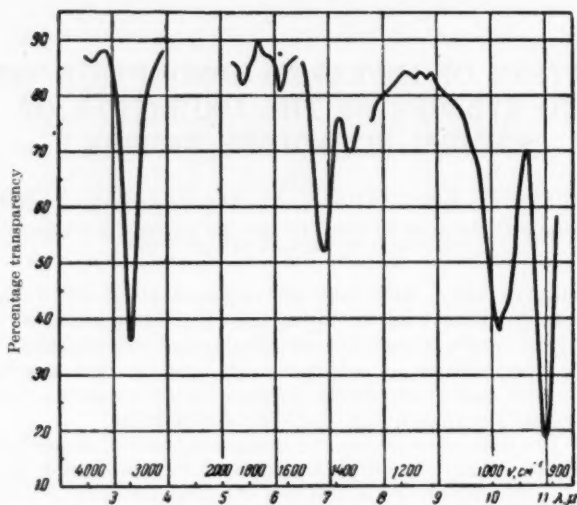


Fig. 1.—Absorption spectrum of unoxidized sodium-butadiene rubber.

oxidation were studied on the same film. The specimens were oxidized in an atmosphere of dry oxygen at 142–145° C for 5, 10, 20, 30, 40, and 60 minutes, respectively.

EXPERIMENTAL RESULTS

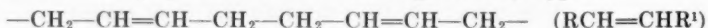
Figure 1 gives the spectrum of unoxidized sodium-butadiene rubber. In the spectrum the following lines are observed: a line about 3.35μ (2988 cm⁻¹) corresponding to the valence oscillations C—H; a line about 6.1μ (1640 cm⁻¹), corresponding to the oscillations C=C; and a line about 6.9μ (1460 cm⁻¹) corresponding to the deformation oscillations of the methylene groups.

In the long wave length portions of the spectrum there are two lines about 10.15μ (985 cm⁻¹) and 11.0μ (909 cm⁻¹), which depend on the C—H deformation

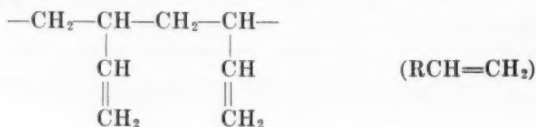
oscillations in the $\text{C}=\overset{\text{H}}{\text{C}}$ group.

In infrared measurements of simple olefins, Thompson and Torkington² established the difference of the spectra of two types of polymers. The 1,2-type, $\text{RCH}=\text{CH}_2$, has lines at 10.1μ (985 cm⁻¹) and 11.0μ (909 cm⁻¹); the 1,4-type, $\text{RCH}=\text{CHR}^1$, has a line at 10.3μ (965 cm⁻¹). Consequently, the position of the lines in the infrared spectrum depends on the distribution of double bonds in the hydrocarbon chain (in the main chain or the side chains).

Butadiene can be polymerized either according to the 1,4-type:



or according to the 1,2-type:



These types are usually found in different proportions in technical products.

In our preparation of sodium-butadiene rubber, the 1,2-type predominated. Consequently there are two lines in the spectrum; 10.15μ (985 cm^{-1}) and 11.0μ (909 cm^{-1}). The presence of a small quantity of 1,4-polymer is shown in the spectrum by the inflection at 10.3μ (965 cm^{-1}).

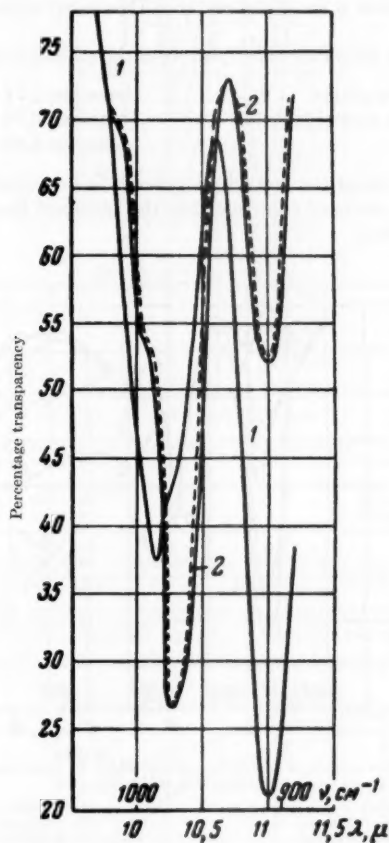


FIG. 2.—Absorption spectra of sodium-butadiene rubber containing polymers of the 1,2-type and 1,4-type in different proportions. (1) Predominantly the 1,2-type. (2) Equal proportions of the two types.

To verify this, we obtained the spectrum of rubber, which contains, according to its reaction with perbenzoic acid, an equal quantity of this polymer and of the other polymer (see Figure 2, note 2). Its infrared spectrum has an intense line at 10.3μ (965 cm^{-1}) and a weaker line at 11.0μ (909 cm^{-1}); the line at 10.15μ is slightly curved.

We shall observe how the spectrum of sodium-butadiene rubber changes during the oxidation process.

Figure 3 gives the spectra of six progressive stages of oxidation of sodium-butadiene rubber. A comparison of these spectra with the spectrum of unoxidized rubber shows new lines resulting from the oxidation process.

Even in the early stages of oxidation, a line is visible at 2.9μ (3450 cm^{-1}), indicating the presence of OH groups. The intensity of this line increases rapidly during the oxidation process. After 20 minutes of oxidation, an intense line appears near 5.8μ (1720 cm^{-1}). This band represents the carbonyl group, $\text{C}=\text{O}$.

Barnes³ gives the following subdivisions of the carbonyl frequency:

for complex ethers	between 5.71 and 5.79μ
for ketones and aldehydes	between 5.79 and 5.81μ
for acids	between 5.90 and 5.98μ

From the character of the line which appears in our spectrum (see Figure 3) at 5.8μ (1720 cm^{-1}), we may conclude that the carbonyl frequencies of all these compounds are present.

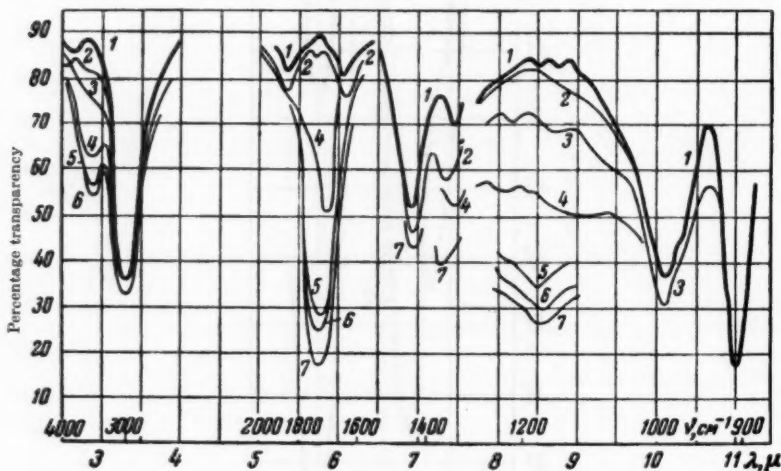


FIG. 3.—Absorption spectra of sodium-butadiene rubber in seven stages of oxidation (unvulcanized rubber).

- | | |
|------------------------------|------------------------------|
| (1) Before oxidation | (5) Oxidation for 30 minutes |
| (2) Oxidation for 5 minutes | (6) Oxidation for 40 minutes |
| (3) Oxidation for 10 minutes | (7) Oxidation for 60 minutes |
| (4) Oxidation for 20 minutes | |

With increase in the time of oxidation, the transparency of part of the spectrum between 7.8μ (1280 cm^{-1}) and 10μ (1000 cm^{-1}) decreases noticeably.

In the later stages of oxidation (around 30 minutes), a line appears near 8.5μ (1170 cm^{-1}) in this region. Thompson relates this region of the spectrum to the oscillations of the $-\text{C}-\text{O}-\text{C}-$ skeleton, which is altered in certain cases by the presence of the carbonyl group, $\text{O}=\text{C}-\text{O}-\text{C}$. To verify this, we photographed the spectrum of a complex ether which gave a broad absorption line around 8.5μ .

The intensity of the lines at 10.15μ (985 cm^{-1}) and 11μ (909 cm^{-1}) decreases noticeably when oxidation is continued. This may be shown by joining those

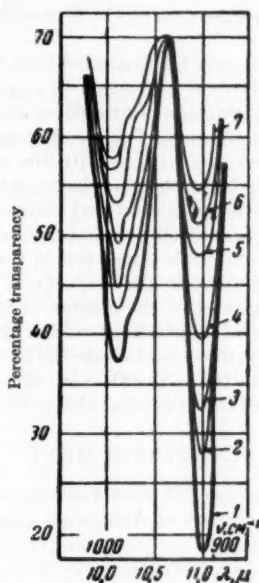


FIG. 4.—Curves of the absorption spectra of sodium-butadiene rubber in the region of lines $\lambda = 10-11\mu$ in relation to the time of heating in the presence of molecular oxygen.

- | | |
|---|------------------------------|
| (1) Before treatment (unvulcanized polymer) | (4) After heating 20 minutes |
| (2) After heating 5 minutes | (5) After heating 40 minutes |
| (3) After heating 10 minutes | (6) After heating 60 minutes |

points on the curves which represent the maximum transparency to correct for the background. On the curves derived by this method (see Figure 4) the intensity of the lines referred to decreases progressively with the time of treatment of the rubber with molecular oxygen. Figure 5 gives the curves of the relation of $\log I/I_0$ for the wave lengths 10.15μ and 11.0μ to the time of oxidation;

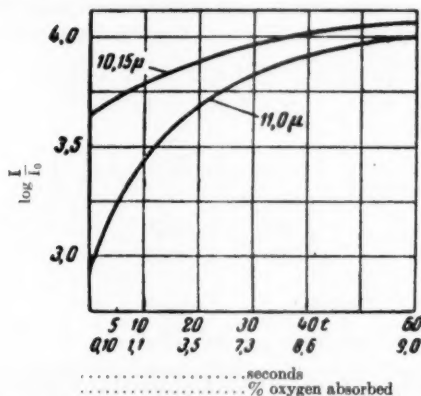


FIG. 5.—Curves showing the decrease in the proportion of double bonds with increase in the time of oxidation.

this indicates a change in proportion of $C=C$ double bonds according to the degree of oxidation.

From the data obtained it may be concluded that the process of oxidation of sodium-butadiene rubber involves a reaction of oxygen at the double bonds. This reaction in the preliminary stage of oxidation, as measured by our method, is at variance with the assumptions of Farmer, Bloomfield, Sundralingam, and Sutton⁴ concerning the reaction of oxygen with the α -methylene groups (with respect to the double bonds in the molecular chains of the rubber).

In any event, a detailed investigation and conclusive evidence concerning this problem would require first of all a comparison of the quantity of oxygen absorbed with the quantity of double bonds lost in the early stage of oxidation.

The formation of such groups as the $-C-O-C-$ and $C=O$ groups explains satisfactorily the character of the change of the physical-chemical and mechanical properties of sodium-butadiene rubber during oxidation. In this connection it is particularly interesting to note the line in the 8.5μ region, which is related to the vibrations in the $-C-O-C-$ skeleton, and which confirms the hypothesis of the union of the molecular chains by means of oxygen bridges.

ACKNOWLEDGMENT

The measurements of the spectra were made in an apparatus belonging to the Y. Y. Mikhailenko Laboratory of Analytical Chemistry, to which we owe our thanks.

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INTERACTION BETWEEN CARBON BLACK AND POLYMER IN CURED ELASTOMERS *

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The improvement of one or more physical properties of vulcanized rubber stocks by the incorporation of a finely divided solid is known as reinforcement. There exist in the literature a number of theories as to the mechanism by which a solid of high surface area, such as carbon black, improves abrasion resistance and increases the tensile strength and the modulus of a cross-linked rubber matrix¹. However, no satisfactory conclusions have been drawn as to the nature of the interaction at the interface between the polymer molecules and the surface of the solid inclusion. In general, it has been considered that van der Waals type adsorption forces are responsible for this interaction². However, there are in the literature a number of references to "chemical binding" between polymer and pigment, usually in reference to carbon blacks³. The work reported here was undertaken to establish more clearly the nature of the interaction between various carbon blacks and the polymer in the cross-linked rubber matrix.

The results of the study are described in three parts:

1. The thermodynamic changes accompanying the extension and retraction of gum and loaded stocks.
2. The chemical nature of the carbon black surface.
3. The relationship of the physical and chemical nature of the carbon black surfaces to the physical properties of the loaded rubber stocks.

THERMODYNAMICS OF RETRACTION OF LOADED STOCKS

The properties of a system may be defined by the thermodynamic equation of state. For the mechanical deformation of rubberlike materials the following equations have been derived⁴:

$$f = \left(\frac{\partial E}{\partial l} \right)_{PT} - T \left(\frac{\partial S}{\partial l} \right)_{PT} + P \left(\frac{\partial V}{\partial l} \right)_{PT} \quad (1)$$

and since

$$\left(\frac{\partial E}{\partial l} \right)_{PT} + P \left(\frac{\partial V}{\partial l} \right)_{PT} = \left(\frac{\partial H}{\partial l} \right)_{PT} \quad (2)$$

and

$$- \left(\frac{\partial S}{\partial l} \right)_{PT} = \left(\frac{\partial f}{\partial T} \right)_{Pl} \quad (2a)$$

then

$$f = \left(\frac{\partial H}{\partial l} \right)_{PT} + T \left(\frac{\partial f}{\partial T} \right)_{Pl} \quad (3)$$

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 1, pages 146-153, January 1951. This paper was presented before the Division of Rubber Chemistry at the 117th Meeting of the American Chemical Society, Detroit Michigan, April 19-21, 1950. The present address of R. S. Stearns is the University of Chicago, Chicago, Illinois.

where f is the force in grams per sq. cm. required to extend 1 cc. of stock to a length, l . The symbols f , E , H , S , P , V , and T represent free energy, internal energy, enthalpy, entropy, pressure, volume, and temperature, respectively. Considerable interest has been shown in the determination of the contribution of the entropy and of the internal energy to the force of retraction of unloaded (gum) stocks⁵. Few data exist, however, to show how these quantities are affected by a finely divided solid⁶.

Equation 3 requires that the tension in a strip of rubber held at constant length should be a linear function of the temperature. That part of the force of retraction which is due to a change in the entropy $\left(\frac{\partial S}{\partial l}\right)_{PT}$, may then be determined from the slope of the isometric, and the enthalpy contribution $\left(\frac{\partial H}{\partial l}\right)_{PT}$, may be determined from the intersection of the isometric with the ordinate at 0° K. If isometrics are determined at a number of elongations, then the integral quantities ΔH , ΔS , and ΔF may be evaluated as the area under the appropriate curve obtained by plotting the differential quantities as a function of the elongation.

Apparatus and method.—The apparatus used to obtain the data necessary to calculate the above quantities was similar to that used by other investigators⁷. A beam balance was mounted on top of an air thermostat, and the motion of the beam was mechanically restricted to ± 0.05 cm. about the rest point. The rubber test-strips were in the form of standard 2-inch dumbbells. The samples were held in the thermostat between two clamps. The upper clamp was suspended from one arm of the balance, and the lower clamp was so arranged that the distance between the two clamps could be varied. The elongation was determined by the distance between bench marks placed on the restricted portion of the dumbbell. The temperature of the air thermostat could be varied from -30° to $+75^\circ$ C, and could be controlled within $\pm 0.1^\circ$ C. The load required to counterbalance the retractive force of the rubber could be read to ± 0.5 gram. The distance between bench marks on the rubber test-strips was determined to ± 0.01 cm. with calipers and a steel scale.

GR-S was used as the medium in which to disperse the pigments since it has no tendency to undergo crystallization on orientation¹⁰. The compounding ingredients added to the polymer to effect cross-linking are listed in Table I. Table II gives the physical properties of the pigments studied.

All stocks in a series containing any one black or other pigment were treated in a like manner. The time of cure was so chosen that the ordinary physical

TABLE I

COMPOUNDING INGREDIENTS

(Stocks cured at 300° F for 60–180 minutes; sample slabs 6 × 6 × 0.075 inches)

	Parts by weight
Sulfur	2.0
Zinc oxide	3.0
Antioxidant ^a	0.5
Accelerator ^b	1.5
GR-S ^c	100.0
Filler or reinforcing pigment	0–45

^a Phenyl-β-naphthylamine.

^b N-cyclohexyl-2-benzothiazole sulfenamide.

^c Stearic acid present to the extent of at least 3.75%.

TABLE II
PHYSICAL PROPERTIES OF FILLERS AND REINFORCING PIGMENTS

	Surface area ^a (sq. meters/ gram)	\bar{d}^b (meters)	r^c
EPC-1 (easy processing channel black)	127	23	0.68 ± 0.1
EPC-2	108	29	0.80
Calcined EPC-2 (black heated to 1000° C. in vacuo)	112	—	—
RF-1 (reinforcing furnace black)	81	29	1.02
RF-2	108	27	1.06
RF-3	218	29	0.44
SRF (semireinforcing furnace black)	19	80	1.00
Graphon (EPC black heated to 3000° C., 6, 7)	76	30	—
(SiO ₂) _m (H ₂ O) _n (precipitated silica)	150	22	0.6

^a Surface area by low temperature nitrogen adsorption⁸.

^b Mean particle diameters from electron micrographs.

^c Ratio of area calculated from electron microscope data to the nitrogen area⁸.

properties, as represented by tensile strength, elongation at break, and modulus at 300 per cent elongation changed only slightly as the time of cure was increased. A plot of the physical properties of rubber stocks against the time of cure shows a rather broad plateau, and the procedure adopted in this work placed all stocks on this plateau, but not necessarily at the same point on the plateau. No use is made of the absolute values of any property, but only of the manner in which the particular property changes with addition of pigment.

Rubberlike materials exhibit several phenomena which make the determination of their physical properties in a state of equilibrium somewhat difficult. In particular, the effects of creep¹¹, permanent set¹² (20), and previous history¹³ must be considered. The effect of the initial deformation on the physical properties of a stock is well illustrated by the data plotted in Figure 1. Here the tension at an elongation of 100 per cent has been plotted as a function of the greatest deformation the test strip has suffered. A period of 1 hour was allowed for relaxation and recovery in these experiments before measuring the force of retraction. The value of l_0 , representing the unstrained length, used to calculate the 100 per cent extension always included the increase in the permanent set introduced as a result of the greater deformation. The cause of this behavior is not clear; it is probably the result of the "untying" of physical

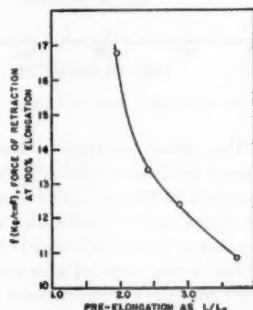


Fig. 1.—Effect of pre-elongation on force of retraction at 100 per cent elongation. GR-S containing 45.0 parts of RF-1 black.

entanglements of polymer chains, the slippage of the adsorbed polymer on the pigment surface, and the possible movement of cross-links along the polymer chain through exchange reactions¹⁴. The stocks were given a known history by allowing them to relax at an elongation of 150 per cent for 1 hour.

The initial relaxation curve at an elongation of 150 per cent and the subsequent recovery curves as the elongation was decreased in increments of 15 per cent are plotted for one typical stock in Figure 2. The initial relaxation curve shows no tendency to reach a constant value, and the rate of relaxation is a

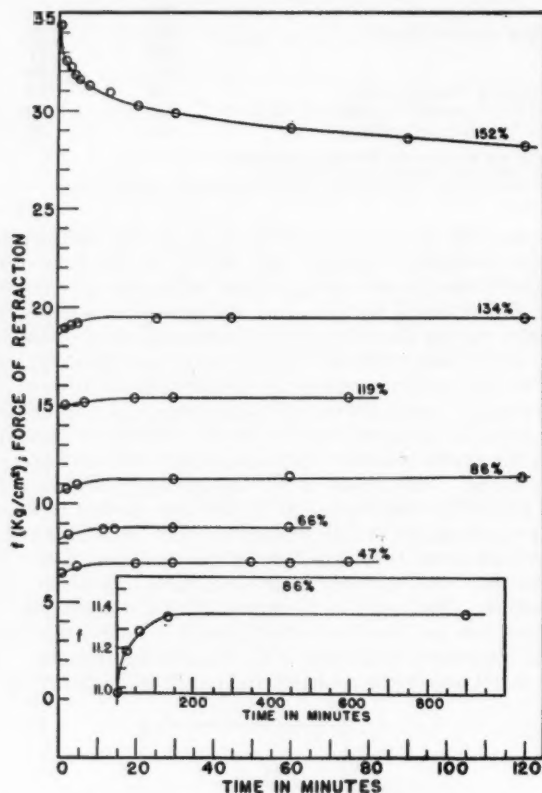


Fig. 2.—Relaxation and recovery curves for GR-S stock containing 37.5 parts of EPC-2 black.

linear function of time in the latter portion of the creep phenomena¹⁵. The authors believe that the linear portion of the relaxation curve is not connected with the physical rearrangement of the polymer chains but is due to the release of tension as a result of the breaking of cross links and oxidative degradation¹⁶. The rate of recovery was found to be rather rapid; at the end of 30 minutes the force of retraction was within 5 per cent of the value which would have been obtained had a much longer recovery period been allowed. This is shown in the insert of Figure 2 where the recovery curve for an extension of 86 per cent has been plotted over a considerable period of time.

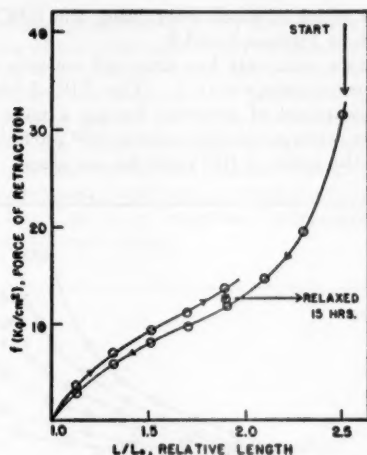


FIG. 3.—Stress-strain curve illustrating hysteresis effect. Stock contained 45 parts RF-1 black in GR-S.

This method of obtaining the stress-strain curves did not eliminate the hysteresis loop as shown in Figure 3. However, the last point on the ascending curve is close, after a relaxation period of 15 hours, to the descending curve, so it would appear that the stress-strain curve obtained by retraction is very close to the true equilibrium curve if such a thing exists for rubber stocks.

Results and discussion.—A typical isometric-tension, as a function of temperature at constant length, of a loaded stock is shown in Figure 4. These isometrics indicate that the force of retraction is a linear function of the temperature over the temperature range covered as required by Equation 3. The slopes of the isometrics were obtained graphically, and the intercepts were calculated by substitution of the value of the slope into Equation 3. The thermodynamic quantities calculated by this procedure for a series of stocks containing

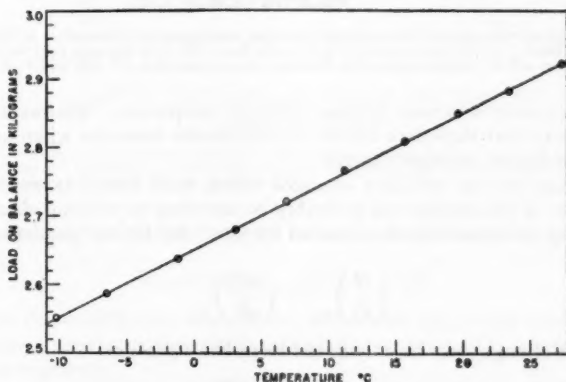


FIG. 4.—Isometric at elongation of 300 per cent for GR-S stock containing 37.5 parts EPC-2 black. Cross-sectional area test-piece, 0.0556 sq. cm.; slope, 0.179 kg./sq. cm. \times °C; intercept, 1.78 kg./sq. cm.

the SRF black and a series of stock containing the EPC-2 black are plotted against the elongation in Figures 5 and 6.

The SRF black has a relatively low area and consists of particles having a mean diameter of approximately 800 Å. The EPC-2 black has an area five times larger and is composed of particles having a mean diameter of 290 Å. The EPC-2 black then contains on the order of 10^{16} particles per gram, whereas the SRF black has of the order of 10^{14} particles per gram. The two blacks are,

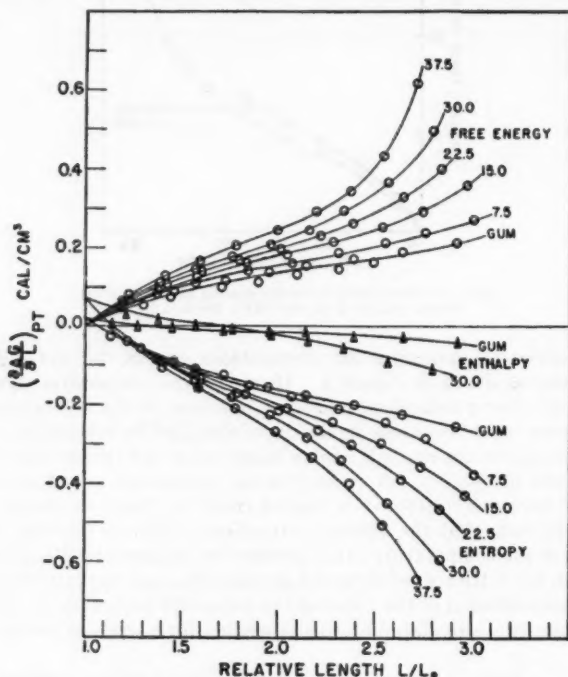


FIG. 5.—Curves representing thermodynamic changes accompanying deformation of GR-S stocks containing EPC-2 black. Numbers on curves refer to parts black/100 parts polymer; only two of six enthalpy curves are shown; ΔG on ordinate represents thermodynamic quantities ΔF , ΔH , and $T\Delta S$.

therefore, entirely different in their physical properties. However, Figures 5 and 6 indicate that these two blacks exhibit similar behavior when incorporated in the cross-linked polymer matrix.

The origin of the enthalpy changes which were found to accompany the deformation of the stocks can probably be ascribed to volume changes taking place during deformation, as discussed by Gee¹⁷ for Hevea gum stocks. Since for rubber:

$$\left(\frac{H}{\partial l}\right)_{PT} \simeq \left(\frac{\partial E}{\partial l}\right)_{PT}$$

the volume change may be calculated from the equation:

$$\Delta V = \frac{K}{3\beta T} \int_{l_0}^l \left(\frac{\partial E}{\partial l}\right)_{PT} dl \quad (4)$$

where K is the isothermal compressibility of the elastomer and β is the linear coefficient of expansion of the elastomer. An increase in the volume should be observed, therefore, on deformation at low extensions; at greater extensions a decrease in volume should be anticipated. The volume change is probably the result of an increase or decrease in the intermolecular spacing (in the absence of crystallization), and Gee has shown that at small extensions the change in the internal energy associated with the volume change is approximately balanced by an equivalent change in entropy, so the force of retraction in the rubber matrix remains the same as if an external hydrostatic pressure has been applied to prevent the volume change.

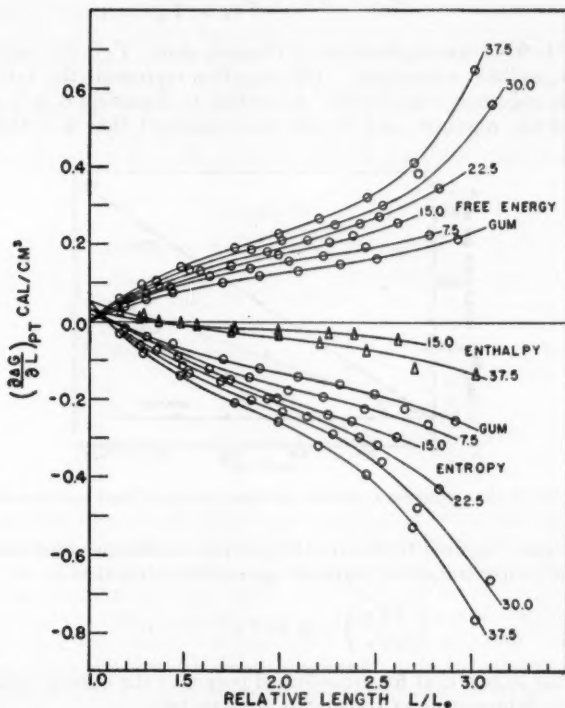


Fig. 6.—Curves representing thermodynamic changes accompanying deformation of GR-S stocks containing SRF black. Numbers on curves refer to parts black/100 parts polymer; ΔG on ordinate represents thermodynamic quantities ΔF , ΔH , and $T\Delta S$.

Assuming that Gee's analysis holds at least qualitatively for GR-S loaded stocks then:

$$W_R = \Delta F = -T\Delta S_d = \int f dl \quad (5)$$

where W_R is the equilibrium work of retraction and ΔS_d is the configurational entropy change accompanying deformation of the matrix due to orientation of the polymer segments.

A large number of isometrics must be obtained to construct the curves presented in Figures 5 and 6. This is a rather laborious procedure, but little

error will be made if the area under the equilibrium stress-strain curve is considered equivalent to $T\Delta S_d$.

A series of GR-S stocks, containing different amounts of the nine pigments listed in Table II, were compounded and the equilibrium stress-strain curves were obtained as previously described. The area under the stress-strain curves from 0 to 125 per cent elongation was evaluated by means of a planimeter and the work of retraction, $[W_R]_0^{125}$, was computed. The work of retraction as a function of concentration is plotted in Figure 7 for several representative pigments. This may be expressed by the equation:

$$W_R = W_R^0 + \phi \frac{V_2}{(1 - V_2)^2} \quad (6)$$

where W_R^0 is the work of retraction of the gum stock, V_2 is the volume fraction of pigment, and ϕ is a constant. This equation represents the data accurately for the nine pigments considered. According to Equation 6, ϕ is an inherent property of the pigment, and it may be considered that ϕ is the additional

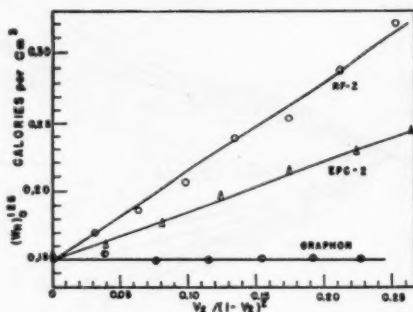


FIG. 7.—Work of retraction as function of volume fraction of black present in stocks.

amount of work required to deform the polymer matrix per unit volume of pigment as the concentration of pigment approaches zero, that is:

$$\left(\frac{dW_R}{dV_2} \right) = \phi \text{ as } V_2 \longrightarrow 0 \quad (7)$$

Wall¹⁸ has shown that for cross-linked polymers the entropy change taking place during deformation of the matrix is given by:

$$\Delta S_d = k \ln \frac{P}{P_0} \quad (8)$$

where P_0 is the number of possible configurations of the polymer chains before deformation and P is the reduced number of possible configurations in the strained state. The following equation may, therefore, be written:

$$W_R = -kT \ln \frac{P}{P_0} + \phi \frac{V_2}{(1 - V_0)^2} \quad (9)$$

where the second term on the right may be considered as representing the further decrease in the entropy of deformation due to the presence of the pigment

as a result of an additional decrease in the number of possible configurations of the polymer segments in the strained state.

Equation 6 may be expanded to give:

$$W_R = W_R^0 + \phi V_2 + 2\phi V_2^2 + 3\phi V_2^3 \dots \quad (10)$$

which has the same form as the equations developed by Rehner¹⁹, Guth²⁰, and Smallwood²¹ to represent the increase in the tensile properties of a polymer when a finely divided pigment is present. The higher terms of Equation 10 represent the effect of particle-particle interaction, and the squared term represents the interaction between pairs of particles.

Table III gives the experimental values of $[\phi]_0$ ¹²⁵ observed for the nine pigments used in this work. It has been considered²² that the variation in the values of ϕ is primarily due to changes in particle shape and degree of aggregation of the particles since, according to Smallwood²¹ and Rehner¹⁹, ϕ should be independent of particle size. This type reasoning might conceivably explain the variation in ϕ among the carbon blacks, but it does not explain the value of zero observed for Graphon and the silica. Also there is no correlation between the surface available for the adsorption of polymer and the value of ϕ —that is,

TABLE III
OBSERVED VALUES FOR CONSTANT ϕ

Pigment	$[\phi]_0$ ¹²⁵ (cal. per cc.)
EPC-1	0.31
EPC-2	0.37
Calcined EPC-2	0.49
RF-1	0.50
RF-2	0.65
RF-3	0.57
SRF	0.46
Graphon	0.00
SiO ₂	0.00

Graphon and silica have a large surface area compared to the SRF black, which in turn has a value of ϕ greater than several of the EPC blacks. It might be argued that the differences in adhesion between the polymer and the surface of the pigment account for the large values of ϕ observed for the seven blacks on the one hand and the zero value observed for the two inorganic pigments on the other hand. However, recent surface work²³ has indicated that there is not a sufficient difference either in the work of adhesion or in the heat of adsorption between the pigments and low molecular-weight hydrocarbons to account for the observation of a value of ϕ equal to zero.

Let it be assumed that the difference in behavior between the carbon blacks and the two inorganic pigments is primarily due to the type of bonding between polymer and pigment. If a chemical bond exists between carbon blacks and the polymer in the cured rubber stocks, the entire carbon black-polymer system could be considered as being cross-linked into a three-dimensional network; if it is assumed that only van der Waals type adsorption forces exist between the silica and the Graphon, then the low values of ϕ obtained from these latter pigments can be understood.

The greater the amount of polymer which is bound or immobilized at the surface of the pigment the larger is the change in S_d on deformation. Beebe²⁴ has pointed out that the heat of adsorption of hydrocarbons on solids is of the

same order of magnitude as the potential barrier to free rotation around single bonds. If these results can be carried over to the polymer system, migration of polymer segments over the surface of pigments would be expected in the cases of physical adsorption of the polymer. This migration of polymer segments would tend to reduce the value of ΔS_d . If, on the other hand, it can be shown that a covalent chemical bond is possible between the polymer and the surface of some pigments, migration of polymer segments could not take place. In this case the polymer could be considered as immobilized, and this would tend to increase the value of ΔS_d . Furthermore, in the derivation of Equation 10, Smallwood²¹ and Rehner¹⁹ considered that the polymer segments are immobilized at the surface of the solid inclusion. This condition cannot be fulfilled if only physical adsorption exists at the polymer pigment interface.

CHEMICAL NATURE OF CARBON BLACK SURFACE

The crystal structure of carbon blacks has been examined in considerable detail²⁵; the adsorption of nitrogen and hydrocarbons on the surface of blacks has yielded much valuable information²⁶; and the morphology of carbon blacks as obtained from electron micrographs is of considerable interest²⁷; but it is only recently that any research has been inaugurated on the chemical nature of the carbon black surface.

It has been known for some time that carbon blacks contain considerable oxygen, hydrogen, and other so-called volatile constituents²⁸. That the pH of carbon blacks depends on the extent of surface oxidation was recognized by Zapp²⁹ and further studied by Villers³⁰. The study of the reaction of the Grignard reagent with carbon blacks undertaken by Villers³¹ has suggested that there exist on the surface of carbon blacks a number of organic functional

groups containing oxygen such as $-\text{OH}$, $-\text{OOH}$, $-\text{C} \begin{array}{c} \text{O} \\ \parallel \\ \text{OH} \end{array}$, and $\text{C}=\text{O}$,

and this is further substantiated by the preliminary work of Smith and Schaeffer³². If, in addition to the above functional groups, evidence could be found

for the existence of ethylenic type bonds $\left[\begin{array}{cc} \text{H} & \text{H} \\ | & | \\ -\text{C} & =\text{C}- \end{array} \right]$ on the surface of car-

on black particles, which may be considered as part of the carbon black structure rather than being present in physically adsorbed organic units, then it may be postulated that, during vulcanization of the carbon black-polymer-sulfur mixture, sulfur cross-links between the polymer and the black occurs, and the black and polymer become combined chemically into a continuous three-dimensional matrix.

The determination of unsaturation is rather difficult and uncertain under the best of conditions. When a large surface, capable of physically adsorbing considerable amounts of reagent, is present, the number of difficulties is not lessened. The problem was solved with some degree of success by the following calorimetric method:

Experimental.—The calorimeter consisted of a silvered Dewar which contained a stirrer, a heater, and a Beckmann thermometer. The entire assembly was immersed in a constant temperature bath. About 10 grams of carbon black, which had been dried in vacuum over calcium sulfate, was dispersed in

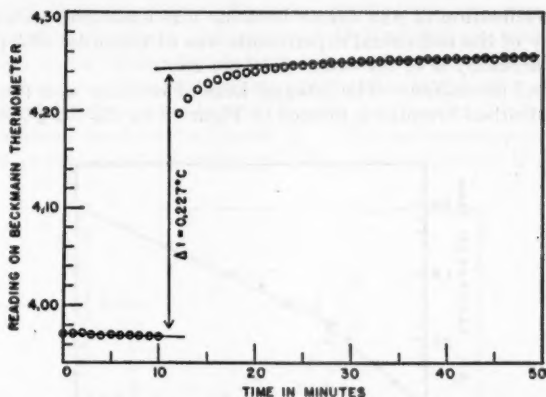


FIG. 8.—Temperature rise on addition of 2×10^{-3} moles of bromine to 10 grams of EPC-1 black in 200 cc. of CCl_4 . Heat capacity of calorimeter was 90.4 cal./°C; ΔH is 2.51 cal./gram of black.

200 cc. of dry carbon tetrachloride and placed in the Dewar. After thermal equilibrium had been obtained, a known amount of bromine dissolved in carbon tetrachloride was introduced by breaking a glass bulb containing the bromine immersed in the black slurry. The type of temperature rise versus time curve obtained is illustrated in Figure 8. After the bromine was introduced, the temperature change was followed for a period of about 1 hour, and the temperature rise was computed by making a linear extrapolation of the temperature-time curve to the instant at which the bromine was introduced as indicated. The heat capacity of the calorimeter was found by passing a known current from a storage battery through the heater of known resistance. The temperature was read on the Beckmann thermometer to $\pm 0.001^\circ \text{C}$ with the aid of a cathetometer. At the completion of the experiments the black was filtered off

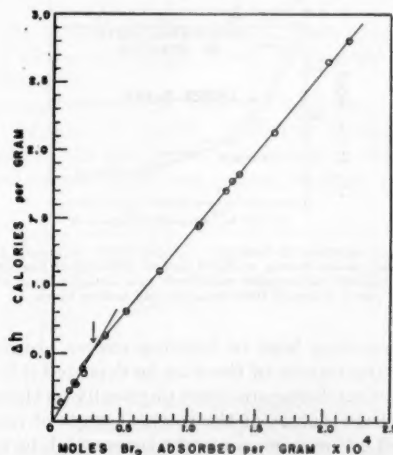


FIG. 9.—Integral heat of reaction of bromine with EPC-2 black.

and the concentration of any excess bromine was measured on a colorimeter. The accuracy of the individual experiments was of the order of 5 per cent and the over-all accuracy is of the order of 10 per cent.

Results and discussion.—The integral heat of reaction as a function of the amount of adsorbed bromine is plotted in Figure 9 for EPC-2 black; Figure 10

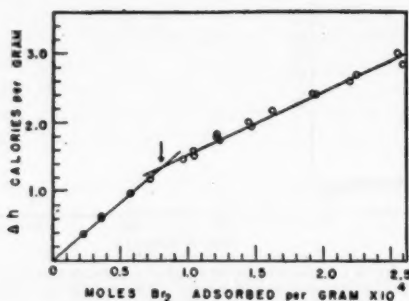


FIG. 10.—Integral heat of reaction of bromine with RF-2 black.

is a similar plot for RF-2 black. It is evident that the integral heat of reaction of bromine with carbon black may be represented by two intersecting straight lines. This is in distinct contrast to the integral heat of reaction curve obtained for Graphon, Figure 11, which is typical of that expected for physical adsorption.

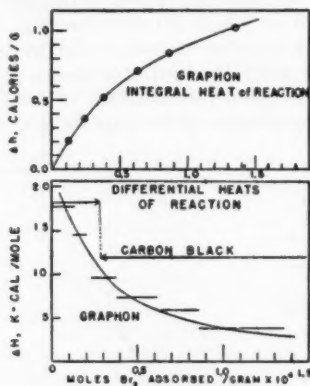


FIG. 11.—Integral heat of reaction for Graphon. Upper curve = integral heat of reaction of bromine with Graphon in CCl_4 slurry; lower curves = chord plot of differential heat of reaction of bromine and Graphon as a function of amount of bromine adsorbed; two straight lines with zero slope = the type differential heat of reaction curve obtained from bromine and carbon black.

The linear and intersecting heat of reaction curves obtained in the case of carbon blacks are characteristic of those to be expected if the bromine is reacting chemically rather than being adsorbed physically on the surface of the black. Figure 12 is a plot of the values of the integral heats of reaction for the seven carbon blacks studied, at bromine concentrations which lie to the left of the discontinuity. The values for six of the seven blacks fall on the same straight line

which passes through the origin. These six blacks have, therefore, an average differential heat of reaction in this region of 18.2 kg.-cal. per mole of bromine. The SRF black has a differential heat of reaction which amounts to 27.5 kg.-cal. per mole of bromine. The equilibrium which exists to the right of the discontinuity, between the free bromine and the adsorbed bromine, follows a Freundlich-type isotherm, as shown in Figure 13. The average slope of the integral heat of reaction curves in this region is 11.9 kg.-cal. per mole of bromine.

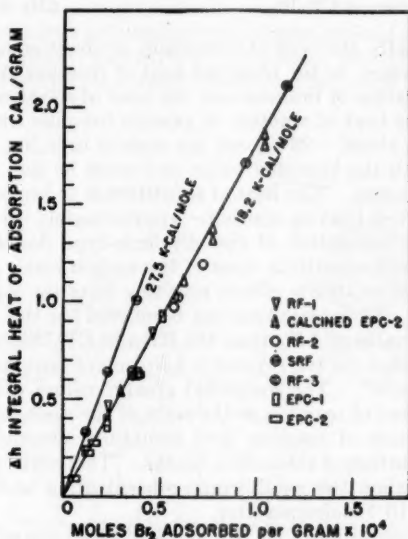


Fig. 12.—Integral heat of reaction for all blacks studied in region below point of discontinuity.

Table IV gives the values of the differential heats of reaction in the regions to the right and left of the discontinuity and the amount of adsorbed bromine at the point of discontinuity.

The heat of reaction of bromine with a double bond in a simple organic molecule is 28 to 31 kg.-cal. per mole²⁰. This heat of reaction refers to the reactants and products in the gas phase. To compare the differential heat of reaction obtained between bromine and carbon black in a carbon tetrachloride

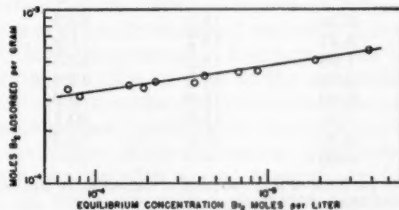
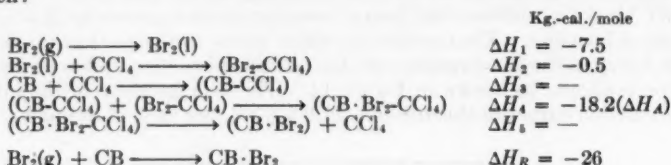


Fig. 13.—Log-log plot of amount of adsorbed bromine against equilibrium concentration of bromine which exists above point of discontinuity.

slurry with the above value the following thermochemical cycle must be written:



It is assumed that ΔH_3 , the heat of immersion, is about equal to ΔH_5 , the heat of emersion. Therefore, to the observed heat of reaction, ΔH_4 , must be added the heat of condensation of bromine and the heat of solution of liquid bromine in the solvent. The heat of reaction of gaseous bromine with carbon black in vacuo, ΔH_R , is then about -26 kg.-cal. per mole of bromine. This figure compares favorably with the expected value and must be due to the addition of bromine to double bonds. The heat of substitution of bromine is considerably less than the observed heat of reaction—approximately 10 to 12 kg.-cal. per mole³⁴. Resonance interaction of the ethylenic-type double bonds with the benzenoid rings, which constitute most of the carbon black particle, should be accounted for as well as steric effects resulting from the strained state of the final configuration. No explanation can be offered for the fact that the SRF black has a greater value of ΔH_A than the RF and EPC blacks.

The heat of reaction for the reversible addition of bromine to phenanthrene is 7.4 kg.-cal. per mole³⁵. The somewhat greater values which were observed as the differential heat of reaction to the right of the discontinuity are possibly due to the equilibrium of bromine with structures resembling phenanthrene which exist on the surface of the carbon blacks. This portion of the curve does not remain linear when the equilibrium concentration of bromine reaches a value greater than 10^{-3} moles per liter.

The point of discontinuity in the plots of the integral heat of reaction against the amount of adsorbed bromine has been taken as a measure of the number of double bonds existing on the surface of the carbon blacks.

A carbon black particle is, according to x-ray evidence, composed of disordered groups of microcrystalline graphite units known as "parallel layer

TABLE IV
HEAT OF BROMINATION DATA

Black	δ^a , Moles/ g. $\times 10^4$	ΔH_A^b , Kg.-cal./ mole	ΔH_R^c , Kg.-cal./ mole	$\delta/\Sigma \delta$, Moles/ sq. meter $\times 10^7$
EPC-1	0.24	18.2	12.2	1.89
EPC-2	0.27	18.2	11.9	2.52
Calcined EPC-2	1.00	18.2	13.3	9.25
RF-1	0.44	18.2	12.4	5.44
RF-2	0.80	17.0	9.2	7.39
RF-3	1.31	18.2	10.1	6.02
SRF	0.36	27.5	13.3	19.0
Graphon	0.00	—	—	—

^a δ = Moles Br_2 adsorbed per gram of black at point of discontinuity assumed to be equivalent to the double bonds existing on the surface of the black.

^b Differential heat of reaction below point of discontinuity.

^c Differential heat of reaction above point of discontinuity.

^d δ expressed as moles per square meter of black surface.

groups". However, elements other than carbon are constituents of carbon black, and it would not seem unreasonable to assume that these elements are situated predominantly at the edges of the carbon planes. On this basis the carbon black particle may be considered as a disordered agglomerate of layers of large polynuclear benzenoid hydrocarbons. A schematic diagram of one such plane is shown in Figure 14. The representation of a carbon black surface as containing various organic functional groups as part of the molecular structure of the particle is useful in correlating many of the properties associated with the material.

The pH characteristic of channel-type blacks arises from the existence of large numbers of hydroxyl and carboxyl groups on the surface of these blacks. The origin of these groups on channel blacks and their lack of abundance on the

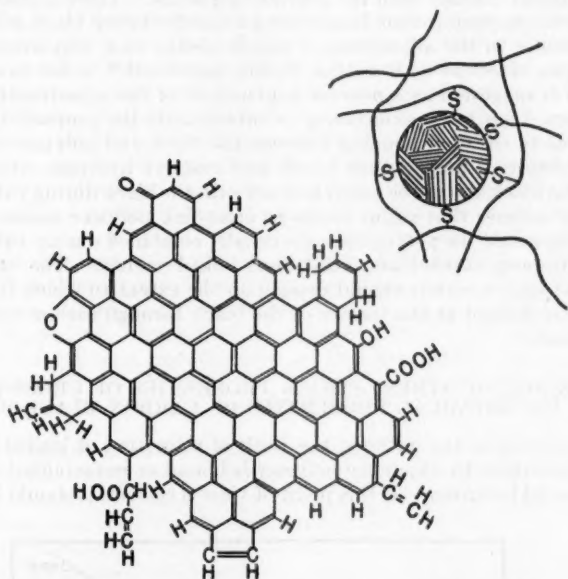


Fig. 14.—Schematic diagram of single plane in parallel layer group of carbon black particles. Various organic functional groups have been placed around edges of polynuclear benzenoid hydrocarbon; figure at upper right = proposed reaction between polymer, sulfur, and carbon black during vulcanization.

surface of furnace blacks is probably the result of the method of preparation of the two types of carbon blacks. Channel blacks are prepared in such a manner that there is free access of newly deposited carbon to the oxygen of the atmosphere at a relatively high temperature. The oxygen can react with the double bonds or active hydrogen atoms to give, as the end product in a series of reactions, the various oxygen-containing functional groups found by Villers²¹. Furnace blacks apparently are formed in an atmosphere deficient in oxygen and are not exposed to the oxygen of the atmosphere until they have been cooled to a temperature where reaction with oxygen is relatively slow. Furnace blacks would be expected, on this basis, to have a larger number of double bonds or active hydrogen atoms per unit surface area than channel blacks. Column 5 of Table IV indicates that the above conclusion is in accord with the experi-

mental evidence. When channel blacks are heated at temperatures between 500° and 1000° C, the oxygen-containing groups are decomposed and removed as carbon dioxide, carbon monoxide, and water. The remaining carbon and hydrogen atoms on the surface undergo rearrangement at these temperatures, and it is therefore not surprising to find that the calcined EPC-2 black has a much greater number of double bonds than the parent black.

The existence of hydroperoxides and α -methylene carbon atoms on the surface of carbon blacks may account for the familiar phenomena of bound rubber—that portion of polymer found to be insoluble after milling polymer and black together. It may be assumed that either the hydroperoxide present in the polymer chains will react to link the polymer to the black through a carbon-carbon bond or that a hydroperoxide group on the surface of the black will react in a similar manner with the polymer segments. There is also the possibility of carbon-oxygen-carbon bonds being formed between black and polymer. If the difference in the adsorption of simple olefins and dihydromyrcene on carbon blacks, observed by Schaeffer, Polley, and Smith³⁶, is due to chemisorption, which is suggested as a possible explanation of the experimental data by these authors, their work would seem to substantiate the proposal that bound rubber is due to covalent bonding between the black and polymer in solution.

The existence of both double bonds and reactive hydrogen atoms on the surface of the black allows the sulfur to react with the black during vulcanization in the same manner that sulfur reacts to cross-link polymer chains. On this basis, the black and the polymer are chemically combined during vulcanization into a continuous three-dimensional cross-linked matrix. The stress-strain properties of such a matrix should depend on the extent to which the polymer has been immobilized at the surface of the black through carbon black-sulfur-polymer bonds.

DEPENDENCE OF STRESS-STRAIN PROPERTIES OF CROSS-LINKED MATRIX ON CHEMICAL PROPERTIES OF CARBON BLACK SURFACE

In the opinion of the authors, the work of retraction of loaded stocks depends on the extent to which the polymer is bound or immobilized at the surface of the solid inclusion. If this point of view is correct, it should be possible

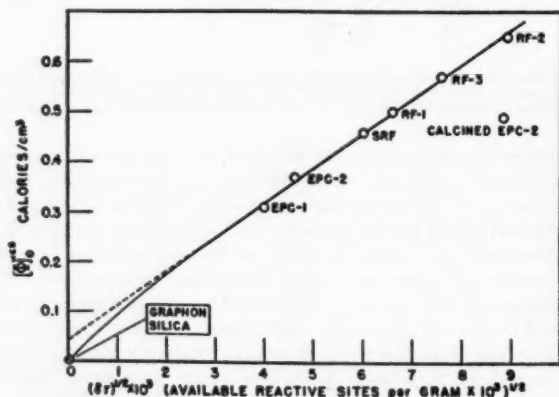


Fig. 15.— G' Plotted against square root of number of available reactive sites per gram of black.

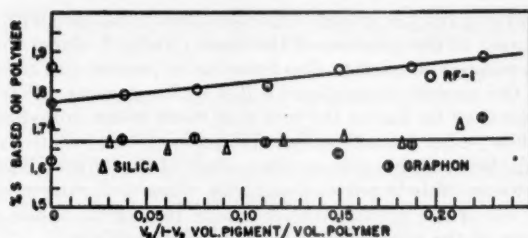


Fig. 16.—Combined sulfur in cured stocks as function of volume fraction of black present.

to express the work of retraction of a polymer-pigment system, as characterized by the constant $[\phi]_0^{125}$, as a function of the number of possible sites on the surface of the pigment where the polymer may be chemically bound. This latter quantity has been derived from the heat of reaction of bromine with carbon black as described. Figure 15 shows the values of $[\phi]_0^{125}$ plotted as a function of the number of available sites for chemical reaction per gram of pigment. In calculating the number of available double bonds it was assumed that some fraction of the total surface area of the pigment is not available for adsorption of polymer. The fraction of the total area which appears as internal area has been taken as $1 - r$, where r is the ratio of the area calculated from electron micrographs to the area obtained from nitrogen adsorption data. Dannenberg and Collyer³⁷ in their work with bound rubber also came to the conclusion that the surface area as measured by nitrogen adsorption was not all available for adsorption of polymer. Except for the calcined EPC-2 black, all the nine pigments examined fall on a smooth curve, so to a first approximation it may be written that:

$$\phi = b(\delta r)^{1/2}$$

where b is a constant and δ is the number of reactive sites per gram of pigment. Thus it is possible to express the effect of a pigment on the elastic properties of a cross-linked matrix as a function of the ability of the pigment to immobilize the polymer at the surface through chemical bonding.

The determination of the amount of combined sulfur³⁸ in vulcanizates containing these blacks has yielded further evidence in support of the concept that carbon black and polymer are bound through carbon-sulfur-carbon bonds into a continuous matrix. Figure 16 shows the percentage of combined sulfur based on the weight of polymer present plotted against the amount of pigment present in the stock per unit weight of polymer. For the carbon black the curve has a positive slope, whereas for Graphon and silica, the amount of combined sulfur remains constant as the amount of pigment is increased. The

TABLE V
AMOUNT OF SULFUR COMBINED WITH PIGMENT

Pigment	Moles sulfur/gram pigment $\times 10^4$
EPC-2	0.39
RF-1	0.55
RF-2	1.17
Graphon	0.00
Silica	0.00

slope of the curve gives the amount of sulfur either combined with the black or combined because of the presence of the black; Table V shows that this value is close to the number of reactive sites found to be present on the black surface. The fact that the amount of combined sulfur is always greater than the number of reactive sites may be due to the fact that some of the cross-links are in the form of disulfide rather than thioether linkages. It may seem somewhat surprising that all the available sites on the surface of the carbon blacks have been utilized. However, this is not unreasonable when it is remembered that accelerator and sulfur are probably in excess in the region of the carbon-black particle because of the adsorptive properties of the surface.

The concept that carbon black is chemically bound to the polymer mainly through sulfur bonds, whereas the inorganic pigments are bound principally through van der Waals type adsorption forces, explains many of the properties of carbon blacks and also the failure of inorganic pigments of equivalent size and area to behave in a manner similar to carbon blacks.

SUMMARY

This research was initiated to determine whether the interaction at the interface between the surface of finely divided solids, such as carbon black, and cured elastomers is primarily physical or chemical in nature. Further, it was desired to correlate some physical property of the reinforced stock with the surface properties of the solid pigment.

Through an examination of the thermodynamic changes accompanying the deformation of loaded stocks it is shown that physical adsorption of the van der Waals type occurring at the interface between pigment and polymer is inadequate to account for the experimental observations. However, if chemical bonding occurs at the interface between polymer and pigment, then the entropy of deformation of the stock may be correlated with the extent of this bonding. By a calorimetric method it was demonstrated that the surface of a carbon black particle contains sites that react with bromine to liberate the same amount of heat as low molecular-weight olefins.

It is, therefore, proposed that a carbon black particle be considered as a disordered agglomerate of polymeric benzenoid type molecules which contain around their perimeters various functional groups. The existence of olefinic-type unsaturation on the surface of carbon blacks suggests strongly that, in the case of carbon blacks, the polymer and pigment are combined chemically through pigment-sulfur-polymer bonds into a continuous three-dimensional cross-linked matrix.

ACKNOWLEDGMENT

The authors wish to thank F. W. Stavely and members of the Firestone Research staff for their interest and assistance in this work, and gratefully acknowledge the helpful discussions with Walter Nudenberg of the University of Chicago and F. T. Wall of the University of Illinois.

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THE DESTRUCTIVE DISSOLUTION OF VULCANIZED RUBBERS*

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In previous work¹ the process of destructive dissolution of vulcanized natural rubber was described, and it was shown that, in the strict absence of oxygen, a vulcanizate cannot be dissolved in a hydrocarbon medium at temperatures up to 140° C. Only in the presence of molecular oxygen does heating bring about dissolution of vulcanized rubber in the solvent, under which conditions the process proceeds along this pattern: union of oxygen with the double bonds → disintegration of the molecular chains where oxygen has combined → dissolution. If the surface area of the vulcanizate remains constant, the process takes place at a constant rate which depends on the temperature and the partial pressure of the oxygen in solution.

In the following, experiments are described, the results of which show that vulcanized synthetic polymers also undergo destructive solution.

The experimental method was the same as that described previously². The vulcanizates were prepared from recipes adapted to the particular synthetic rubbers. As was expected, the rate of destructive solution depends on the molecular structure of the rubbers (see Figure 1).

Based on the increase of the rate of solution, the vulcanized polymers can be arranged in the following order: Butyl rubber < sodium-butadiene < butadiene-styrene copolymer < polychloroprene < natural rubber. For the polymers which do not contain electrophilic groups in their molecules, this order corresponds to the concentration of double bonds in the main chains of the polymer. The presence of electrophilic groups slows down the process of oxidative destruction. Thus, vulcanized polychloroprene dissolves more slowly than does vulcanized natural rubber, although the double bond content in the molecular chains of both the elastomers is identical.

It is important to note that the double bonds which are located in the vinyl side-chain groups of the molecular chains of the polymer play no part in the destructive solution of the vulcanizates.

This is explained on the basis of two facts. First, the side groups do not enter into the composition of the spatial structure characteristic of the vulcanizate, the disintegration of which causes solution. Second, as has already been shown by one of us³, the reaction of oxygen with the vinyl side-chain groups causes a reformation of the structure of the polymer, that is, reverses the process.

The importance of the different positions of the double bonds in the molecular chains of the polymer during destructive solution is clearly shown by butadiene polymers which contain different proportions of 1,4-structure (double bonds in the main chains) and 1,2-structure (double bonds in the side vinyl groups). Polymers were prepared which, according to the data of the kinetics of their

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alan Davis from the *Reports of the Academy of Sciences, USSR*, Vol. 73, No. 4, pages 701-704 (1950).

reaction with perbenzoic acid (Prilejayer reaction) contained 59, 54, and 43 per cent of 1,4-structures. The vulcanizates were prepared according to a single recipe from vulcanized natural rubber, in which the content of 1,4-structures is 100 per cent. Figure 2 shows that the rate of destructive solution of these vulcanizates is a linear function of the content of double bonds in the main chains (1,4-structures). The fact that the curve which shows the relation of the rate of solution to the number of 1,4-double bonds does not pass through the origin indicates that the double bonds in the side-chain vinyl groups of the 1,2-structure of the polymer cause a reverse reconstruction process. When the concentration of oxygen in the system is constant (the partial pressure of oxygen in the solvent was constant), the kinetics of the system can be determined, thus:

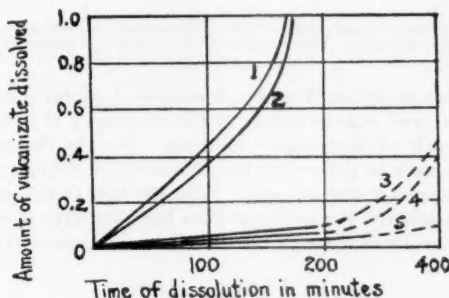


FIG. 1.—Curves showing the kinetics of the destructive solution of vulcanized rubbers at 110° C and under a pressure of oxygen of 760 mm. (1) Natural rubber; (2) polychloroprene; (3) butadiene-styrene copolymer; (4) sodium-butadiene rubber; (5) Butyl rubber.

the rate of disintegration of the molecular chains v_1 is proportional to the concentration c of double bonds of the 1,4-type.

$$v_1 = k_1 c \quad (1)$$

but the rate v_2 of the processes of reconstruction is proportional to the concentration, $c_2 = (1 - c)$, of double bonds of the 1,2-type.

$$v_2 = k_2 (1 - c) \quad (2)$$

Then the average rate of destructive solution is represented by the algebraic sum of the rates of both processes:

$$V = v_1 - v_2 = -k_2 t (k_1 - k_2) c \quad (3)$$

As was shown earlier⁴, the process of solution proceeds in the surface layer at a fixed rate which depends on the initial concentration of double bonds. For this reason Equation (3) applies to the whole process if the surface area of the destroyed vulcanizate is constant. The constants of Equation (3) depend on the temperature, the partial pressure, and coefficient of oxygen in the solvent. For solution in oxylene of vulcanizates which contain as the accelerator, tetramethylthiuram disulfide, when $p = 760$ mm., $t = 120^\circ$, Equation (3) appears thus:

$$V = -4 \times 10^6 + 1.2 \times 10^{-7} c \quad (4)$$

where V is expressed in g./sq. cm./min. and c is the percentage of double bonds in the 1,4-structure, based on the total double-bond content of the polymer.

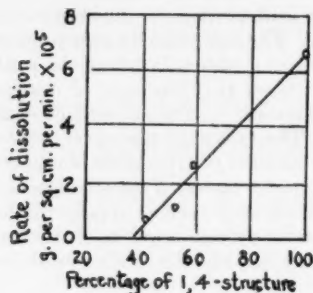


FIG. 2.—Relation of the rate of destructive solution of vulcanized butadiene polymers to the content of 1,4-type of structure. Temperature 120° C. Pressure of oxygen 760 mm.

The relationship established makes it possible to determine experimentally the content of 1,4- and 1,2-structures in the molecules of butadiene polymers according to the rate of destructive solution. For the determination of this value, it was necessary to determine the temperature change of the coefficient of absorption of oxygen in the solvent. With the help of the method which has been described elsewhere⁵, it was found that the solubility of oxygen in xylene at increasing temperatures from 23° to 100° C increases according to the following linear equation:

$$I_A^T = 150.5 + 0.395t \quad (5)$$

The kinetics of solution of the vulcanizate conform to the equation:

$$dKa/dT = k[O]S \quad (6)$$

where $[O]$ is the concentration of oxygen in the solvent and S is the surface area of the vulcanizate. If the calculations of $[O]$ according to Equation 5 are incorporated in this equation, the kinetic constants obtained conform to the Arrhenius equation (see Figure 3). The actual energy of activation of destructive solution of vulcanized natural rubber in the temperature range of 87–107° C is 19 kcal. per mole⁶; for the vulcanizate of sodium-butadiene rubber in the temperature range of 108–132° C it is 31.3 kcal. per mole, and for butadiene-styrene copolymer it is 27.2 kcal. per mole.

The significant increase of the energy of activation in passing from natural rubber to butadiene polymers is explained by the presence in these polymers of

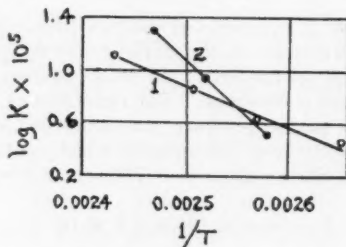


FIG. 3.—Effect of temperature on the kinetic constants in the destructive dissolution of different types of vulcanizates. (1) Sodium-butadiene rubber. (2) Butadiene-styrene copolymer.

double bonds in the side-chain vinyl groups, which direct the process toward a spatial structure formation.

Destructive dissolution of vulcanized sodium-butadiene rubber leads to the formation of a yellowish opalescent solution. Methyl alcohol precipitates from solutions of concentrations of not less than 5 per cent about 70 per cent of the product as a sticky mass, which, after drying in a vacuum at 20° C, can be completely dissolved in all ordinary solvents of rubber.

Chemical analysis of the product of the destroyed vulcanizate shows that it contains free carboxyl groups (5.4 mg. of carboxylic oxygen per gram of vulcanizate), ether groups (12 mg. of oxygen per gram of vulcanizate), and peroxide groups (1.2 per cent of the active oxygen). The total oxygen content in the product of the destroyed vulcanizate after precipitation with methyl alcohol was ~4.0 per cent.

The particle weight of the destroyed vulcanizate was determined by the cryoscopic method with benzene solutions of concentrations not less than 2 per cent. The values lay between 3600 and 2400, and a tendency of the particle weight to increase with decreasing concentration of the solution was observed.

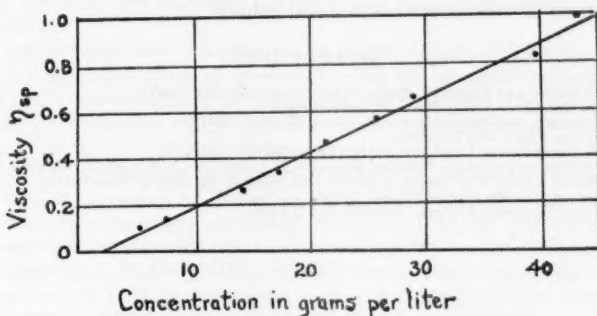


FIG. 4.—Relation between the viscosity of destructively dissolved sodium-butadiene rubber and the concentration.

The osmotic particle weight, extrapolated to a concentration 0, is ~16000. Undoubtedly this particle weight is characteristic of a high molecular fractionation of the product as a result of permeability of the membrane to low molecular fractions.

The viscosity of the xylene solution of a destructively dissolved vulcanizate of sodium-butadiene polymer within wide limits of concentration conforms to the following linear relationship:

$$\eta_{sp} = 24.0vc \quad (7)$$

where v is the specific volume of the vulcanizate and c is the concentration in grams per liter. The numerical coefficient of the equation makes it possible to calculate according to the table of Simha⁷ the ratio of the axes of the ellipsoid of revolution, corresponding to the volume of the particles of the destroyed vulcanizate. This ratio is 15. For molecules of raw sodium butadiene-rubber⁸ it is 65.

The coefficient of Equation 7 is approximately ten times as large as the numerical coefficient of the Einstein equation, which proves that the effective

volume of the particles of the destructively dissolved vulcanizate is ten times as great as their volume in the solid state. The results show that the initial volume of the vulcanizate in xylene increased in the ratio of 8.5:1. From a comparison of these values it follows that large particles which swell in a solvent like fragments of the original spatial structure of the vulcanizate are contained in the solution of destructively dissolved vulcanizate. The very disintegration of this spatial structure of the vulcanizate is a consequence of the oxidizing processes which cause rupture of the molecular chains of the rubber mainly where peroxide groups appear. Such a mechanism of degradation is confirmed by the discovery in the dissolved products of a significant proportion of carboxyl groups. Besides the destructive processes in rubbers that contain part of their double bonds in the form of vinyl side-chain groups, there are processes which lead to the formation of spatial structures and which involve to a considerable degree secondary reactions between the functional oxygen-bearing groups (the reactions of esterification, confirmed by direct analytical data) and there are also polymerization processes which are initiated by the peroxides formed during oxidation. As a result of these latter reactions, a retardation is evident in the dissolution of the synthetic-rubber vulcanizates mentioned when compared to the dissolution of vulcanizates of natural rubber.

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PRIMARY CREEP AND STIFFNESS OF VULCANIZED RUBBERS *

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Primary creep is the subject of a comprehensive work by Leaderman¹, in which there are numerous references to rubber, but time has not permitted the publication here of normalized creep and recovery curves on which further analysis along those lines of thought would depend.

Leaderman includes typical creep curves for a hard and a soft rubber. This paper, on the other hand, shows that at room temperature the shape of the creep curve depends on some or all of the ingredients in the basic mix, probably including the polymer, but only to a very small extent on the reinforcing black.

The results form part of a program of development work on the stiffness of rubber springs. The work is concerned with the accurate determination of load-deflection curves and with predicting the deflection and the subsequent slow change in deflection which together result from the application of a steady load. Such data are required not only for the design of rubber components but also for process control and acceptance tests on finished products.

The gradual increase of deflection of a specimen under constant load is known commonly as creep, and that component of the deflection which is wholly recoverable after removal of the load has been called primary creep¹ or delayed elasticity. In the present work all the deformations have a recoverable component which is large compared with the nonrecoverable component or permanent set, and the latter has consequently been neglected in quoting results.

Generally speaking, the deflection in a rubber spring under load depends on the compounding and processing of the rubber, the temperature of the test, the shape and size of the test-specimen, the geometry of loading, *i.e.*, compression, tension, shear, bending, etc., the load history, and the previous history of the specimen. Experimental work has been carried out to study the effect of these variables and of the interaction between them.

The distinguishing feature of the main experiment lies in the fact that of a number of small cylindrical specimens, some have been loaded in tension and compression, while others have been loaded in shear to give values of the deflection after 1 minute and of the change of deflection during subsequent days. In short, results show the influence of most of the variables mentioned above on stiffness and primary creep.

EXPERIMENTAL WORK

Compounding, molding, and curing.—Four basic mixes were employed: (1) a highly resilient natural rubber mix cured with sulfur and accelerated with Santocure (reaction product of cyclohexylamine and mercaptobenzothiazole) and

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 365-373, February 1951. This paper was presented at the International Meeting of the Division of Rubber Chemistry of the American Chemical Society, Cleveland, Ohio, October 11-13, 1950.

tetramethylthiuram disulfide; (2) a natural rubber bonding mix, cured with sulfur and accelerated with mercaptobenzothiazole; (3) a Neoprene Type GN mix cured with zinc oxide and lightly calcined magnesia, and (4) a Hycar OR-15 mix cured with sulfur.

A highly resilient natural-rubber mix was compounded with lampblack and the other mixes with equal quantities of gas black and lampblack (Table I).

All compounds were mill-mixed; the hard and medium Neoprene compounds were extruded as 0.5-inch bar first, but all samples were ultimately press-cured in a six-cavity compression mold.

Each specimen was first cured for 20 minutes at 153° C, rested for 3 days, and tested. Some specimens were then given a second cure of 20 minutes at 153° C and allowed to rest 3 days before testing.

TABLE I
BASIC MIXES
(Parts of carbon black per 100 parts of rubber)

Compound	GEC ^a Black	Micronex MPC ^b
1. Resilient natural rubber gum stocks	0	0
Resilient natural rubber soft	10	0
Resilient natural rubber medium	37	0
Resilient natural rubber hard	98	.0
2. Bonding natural rubber gum stock	0	0
Bonding natural rubber soft	20.9	20.9
Bonding natural rubber medium	36	36
Bonding natural rubber hard	82	82
3. Neoprene gum stock	0	0
Neoprene soft	7	7
Neoprene medium	25.6	25.6
Neoprene hard	43.2	43.2
4. Hycar gum stock	0	0
Hycar soft	3.5	3.5
Hycar medium	28	28
Hycar hard	5	5

^a General Electric Co. lampblack.

^b Micronex medium process carbon gas black.

Temperature control.—All tests were carried out at a controlled temperature of 21° ± 1° C.

Shape and size of test-specimens.—To study the phenomenon of primary creep, the load is required to change instantaneously from zero to the required load—a condition that can be approached in practice only by applying the load within a time interval which is short compared with the time that elapses before the first reading. Many engineering problems would arise in attempting to apply a load of, say, 150 pounds per square inch in 2 seconds, unless the specimens were limited to 0.5 square inch in cross section.

A relatively long specimen is often unstable in compression and always subject to bending when loaded in shear, so it is desirable to keep the diameter-height ratio of a standard test specimen to above 1.5. The height of the specimen is, therefore, restricted to about 0.5 inch and measurements to 0.0005 inch allow the strain to be measured to 0.1 per cent.

The test-specimens used throughout the main test were in fact cylinders ap-

proximately 0.5 inch in height and 0.5 square inch in area of cross-section, having a metal end-piece bonded to each end. To determine the influence of shape on stiffness, a few cylinders 2 inches in diameter were also used.

Geometry of loading.—The specimens were of such proportions that they could be loaded in compression, tension, or shear and resulting deflections conveniently measured.

Load history.—In the main experiment, the load was in the form of a hanging weight whose application required never more than 2 seconds; it was applied to each specimen at zero time and maintained in most cases for one week.

Previous history of specimen².—In recognition of the possibility that specimens tested more than once might soften because of filler breakdown, this effect was eliminated by straining the specimens before the test slightly above the limits worked to during the test. In earlier work it was found that this precaution enabled results to be repeated within the required accuracy.

TESTING

To begin with, each specimen was tested twice: first in tension, then in compression; or first in compression, then in tension; or twice in shear. Any small

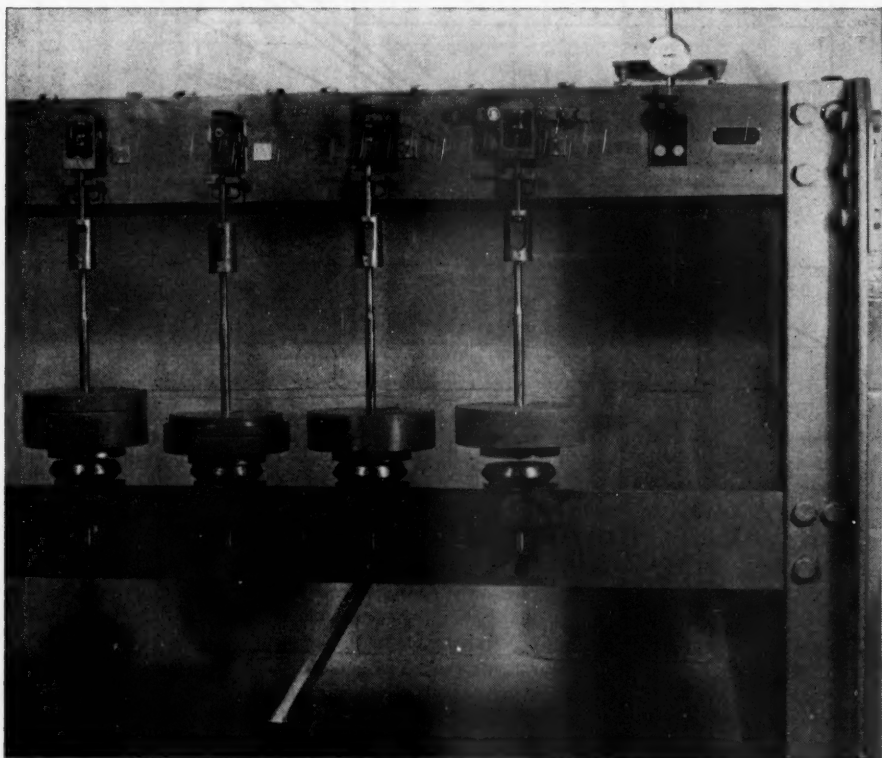


FIG. 1.—Creep apparatus.

permanent extension which occurred during a prolonged test in tension was nullified during a similar test in compression, and vice versa. Permanent deformation in shear was reduced by ensuring that during the second test the direction of the load was reversed by rotating the specimen. Between tests, specimens were allowed to recover.

After being tested twice, certain specimens were given an additional cure, rested again, and retested according to the above plan.

The equipment used for the application of the load and for the measurement of deflection has been described³, but Figure 1 shows four of the twenty-four

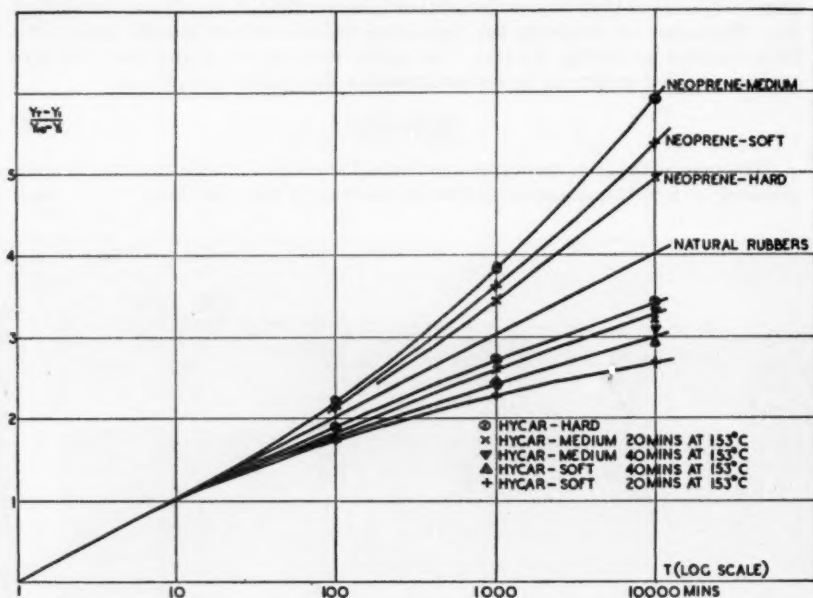


FIG. 2.—Ratio of creep after t minutes to creep after 10 minutes vs. time.

heads available, which, reading from left to right, carry one bonded specimen in compression, one in shear, one in tension, and one unbonded lubricated specimen in compression.

A dial gauge carried on a geometric mounting of the dimple, slot, and plane type enabled deflections to be read to 0.001 inch; the fourth place of decimals, however, could be estimated. In the photograph it is seen in contact with an anvil on which its zero is checked.

The height and diameter of the specimen were measured at the start of each test. One end of each bonded specimen was then bolted to a bracket on the framework, and a stirrup was fixed on the other end. At zero time, a weight was lowered onto the specimen by means of the hand lever shown in the photograph. Readings on the dial gauge were taken once before applying the load and afterward according to a time schedule of 0.3, 1, 3, 10, 30 etc., minutes up to approximately 30,000 minutes or 3 weeks.

NOMENCLATURE

- t = time in minutes after application of load
 Y_t = deflection in inches measured t minutes after application of load
 Y_1 = 1-minute deflection
 $Y_t - Y_1$ = t -minute creep
 $r = \frac{Y_t - Y_1}{Y_1}$ = relative creep
 H = unstrained height of specimen

CHARACTERISTIC CREEP CURVES OF POLYMERS

When a number of different compounds were compared, it was found that the curve of deflection, Y_t , against $\log t$ had a characteristic shape for each polymer. Thus, the deflection of natural rubber test-specimens is proportional to $\log t$ over a wide range of loads, and throughout all these tests no departure from proportionality was observed. The deflection of Neoprene specimens is not

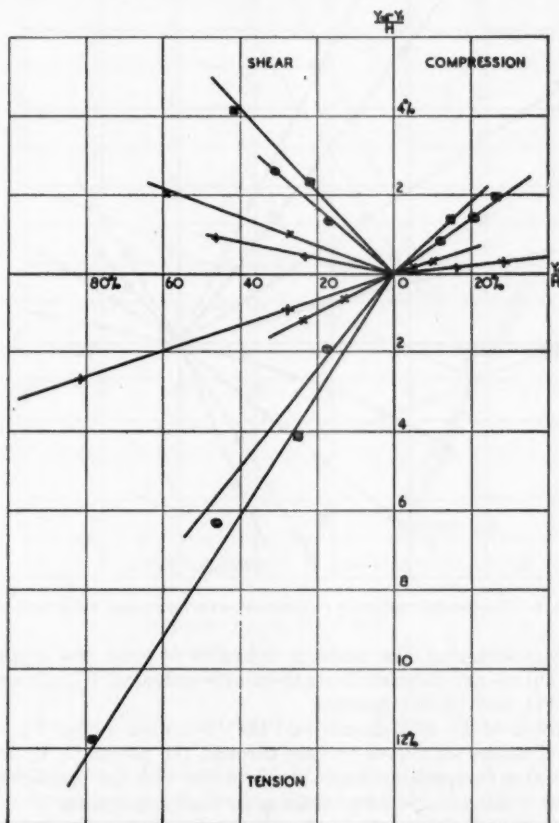


FIG. 3.—Ten-minute creep strain vs. 1-minute strain for soft compounds.

proportional to log time, but the slope of the curve increases slightly with time, whereas that of the Hycar curve diminishes.

To compare the primary creep of one compound with another, it is convenient to use the 1-minute deflection, Y_1 , as the datum from which creep is measured, and to plot the ratio of creep during first t minutes to creep during first 10 minutes [$= (Y_t - Y_1)/(Y_{10} - Y_1)$] against t (log scale) as in Figure 2.

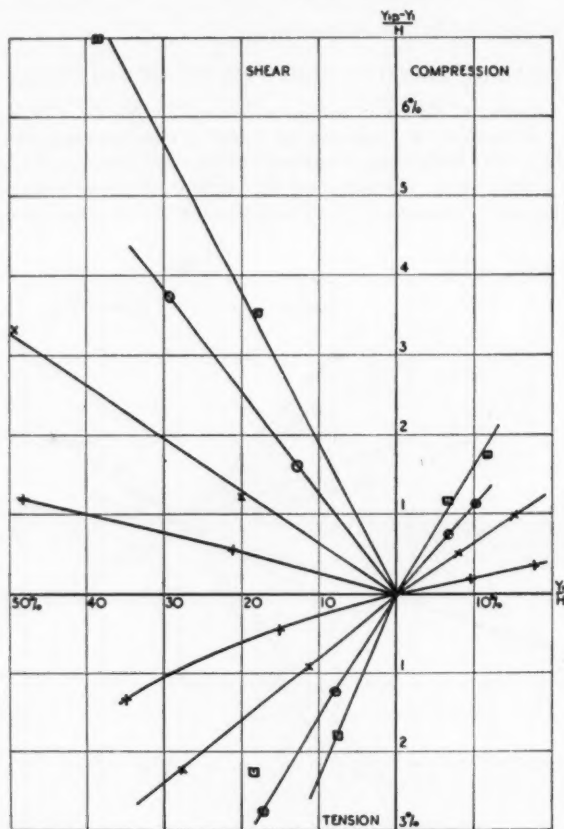


FIG. 4.—Ten-minute creep strain vs. 1-minute strain for medium compounds.

Further simplification has made it desirable to omit the original ten or eleven point curves and to quote from them only values of Y_t , corresponding to 1, 10, 100, 1000, and 10,000 minutes.

The adoption of Y_1 as a datum and the 10-minute creep, $Y_{10} - Y_1$, as a reference level causes all curves to pass through the points (1, 0) and (10, 1); the method makes comparison simple and is in line with the practice of measuring deflections 1 minute and 10 minutes after load application.

Because with these curves the creep, $Y_{10} - Y_1$, during the first 10 minutes of a test can be used to determine subsequent creep, results are given below in

terms of $Y_{10} - Y_1$ for Neoprene and Hycar and in terms of $(Y_t - Y_1)/\log t$ ($= Y_{10} - Y_1$) for natural rubber.

Values of 10-minute creep strain for all compounds can be shown experimentally to be proportional to 1-minute strain (Figures 3, 4, and 5) and one

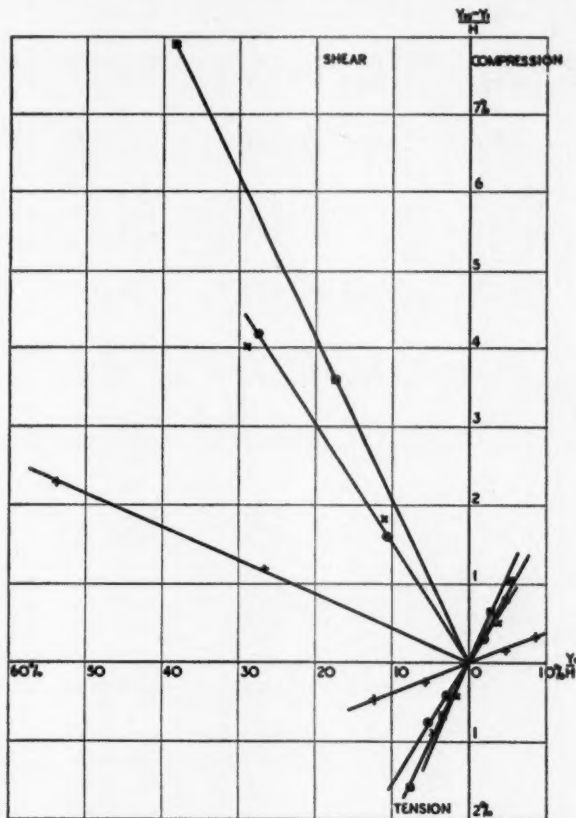


FIG. 5.—Ten-minute creep strain vs. 1-minute strain for hard compounds.

may write:

$$\text{In shear, } Y_{10} - Y_1 = r_s Y_1$$

$$\text{In tension, } Y_{10} - Y_1 = r_t Y_1$$

$$\text{In compression, } Y_{10} - Y_1 = r_c Y_1$$

where $r = (Y_{10} - Y_1)/Y_1 =$ relative creep. Values of r are given in full in Table II.

Influence of cure.—The values of $(Y_t - Y_1)/(Y_{10} - Y_1)$, shown in Table III, are for specimens cured for 20 minutes at 153° C. They were measured again on specimens that had been subjected to an additional cure of 20 minutes, with the following results. For natural rubber bonding compounds, the

TABLE II
VALUES OF LOAD, 1-MINUTE STRAIN AND 10-MINUTE CREEP

Geometry of loading	Soft compounds				Medium compounds				Hard compounds			
	Cure 20 min.				Cure 20 min.				Cure 20 min.			
	Load/ original (lb./sq. in.)	1-min. strain 100 Y_1/H	10-min. relative creep $Y_{10}-Y_1$ $Y_1 \log t$	Cure 20 + 20 min. relative creep $Y_{10}-Y_1$ $Y_1 \log t$	Load/ original (lb./sq. in.)	1-min. strain 100 Y_1/H	10-min. relative creep $Y_{10}-Y_1$ $Y_1 \log t$	Cure 20 + 20 min. relative creep $Y_{10}-Y_1$ $Y_1 \log t$	Load/ original (lb./sq. in.)	1-min. strain 100 Y_1/H	10-min. relative creep $Y_{10}-Y_1$ $Y_1 \log t$	Cure 20 + 20 min. relative creep $Y_{10}-Y_1$ $Y_1 \log t$
Natural rubbers												
Compression	69.2	16.1	0.0155	—	72	9.71	0.0216	—	74.2	4.78	0.0318	—
Compression	130	27.9	0.0150	—	137	17.7	0.022	—	142	8.72	0.0364	—
Tension	72	28.1	0.0321	—	75	15.3	0.0267	—	70	5.93	0.0388	—
Tension	137.2	82.4	0.0320	—	138.5	35.0	0.0378	—	133.5	2.55	0.0416	—
Shear	16.4	23.45	0.0193	—	26.8	21.0	0.0273	—	72	25.6	0.0464	—
Shear	33.6	46.25	0.0211	—	58.0	48.3	0.0248	—	138	53.7	0.0428	—
Compression	21.2	5	0.0337	0.03055	70	7.95	0.064	0.0723	68	1.942	0.1558	0.271*
Compression	43.2	10	0.0329	0.0273	133.5	15.38	0.0558	0.0536	128.7	3.7	0.1437	0.146
Tension	43.2	13.2	0.0458	0.0528	69.2	11.2	0.0821	0.0943	68	1.87	0.2285	0.1865
Tension	62.4	21.5	0.0384	0.0354	131.6	21.8	0.0737	0.1026	130.5	4.79	0.1887	0.1818
Shear	21.6	26.8	0.0382	0.0356	31.6	20.3	0.057	0.057	138	11.18	0.1632	0.1850
Shear	43.2	58.6	0.0352	0.0304	69.7	49.3	0.068	0.0753	130	20.2	0.1360	0.1625
Neoprenes												
Compression	71.2	12.08	0.0703	0.0637	71.6	6.78	0.1162	0.1012	67.8	1.875	0.167	0.172
Compression	136	20.5	0.0703	0.0587	136.7	10.21	0.1126	0.1024	127.8	4.88	0.136	0.135
Tension	71.2	17.61	0.1068	0.1064	71.6	8.00	0.1517	0.1364	67.8	2.82	0.161	0.099
Tension	136	46.2	0.1350	0.13	136.7	17.30	0.1627	—	131.5	5.50	0.154	—
Shear	17.26	16.75	0.0844	0.0759	32.5	12.5	0.130	0.1117	67.8	11.0	0.1465	—
Shear	32.4	30.4	0.0879	0.0805	71.6	29.25	0.124	—	128	27.55	0.1526	—
Hycars												
Compression	72	14.83	0.0944	0.0622	70.0	6.73	0.1772	0.1456	69.0	2.74	0.228	—
Compression	134	26.75	0.0752	0.0748	133.5	11.68	0.1503	0.1214	132.0	5.40	0.190	—
Tension	71.5	25.3	0.162	0.1061	71.2	7.75	0.229	0.1752	69.9	3.43	0.287	—
Tension	139	79.3	0.1752	0.1082	135.5	18.40	0.222	0.174	133.8	7.92	0.227	—
Shear	17.4	21.9	0.108	0.0803	31.9	17.98	0.198	—	69.2	17.85	0.202	—
Shear	32.7	40.8	0.102	0.0767	70.2	38.80	0.181	—	132.5	38.50	0.202	—

* Improbable value.

TABLE III
VALUES OF t -MINUTE CREEP/10-MINUTE CREEP

t , min.	Log t	Neoprene, soft				Neoprene, medium				Neoprene, hard			
		Y_t	$\frac{Y_t - Y_1}{Y_{10} - Y_1}$	Y_t	$\frac{Y_t - Y_1}{Y_{10} - Y_1}$	Y_t	$\frac{Y_t - Y_1}{Y_{10} - Y_1}$	Y_t	$\frac{Y_t - Y_1}{Y_{10} - Y_1}$	Y_t	$\frac{Y_t - Y_1}{Y_{10} - Y_1}$	Y_t	$\frac{Y_t - Y_1}{Y_{10} - Y_1}$
1 10 100 1,000 10,000	0	0.0583	—	0.0992	—	0.0327	—	0.0488	—	0.0093	—	0.0175	—
	1	0.0624	1.0	0.1062	1.0	0.0365	1.0	0.0543	1.0	0.0109	1.0	0.0199	1.0
	2	0.0673	2.105	0.1143	2.029	0.0412	2.237	0.0607	2.164	0.0127	2.154	0.0225	2.113
	3	0.0733	3.659	0.1213	3.157	0.0461	3.526	0.0685	3.582	0.0146	3.372	0.0255	3.374
	4	0.0803	5.366	—	—	0.0520	5.080	0.0780	5.309	—	—	0.0292	4.916
1 10 100 1,000 10,000	0	0.0862	—	0.229	—	0.0382	—	0.083	—	0.0143	—	0.0253	—
	1	0.0954	1.0	0.260	1.0	0.0440	1.0	0.0965	1.0	0.0166	1.0	0.0292	1.0
	2	0.1065	2.207	0.297	2.19	0.0511	2.222	0.114	2.29	0.0191	2.087	0.0335	2.103
	3	0.1216	3.848	0.346	3.78	0.0602	3.79	0.137	4.00	0.0217	3.217	0.0394	3.615
	4	0.1419	6.054	0.394	5.34	0.0710	5.66	0.167	6.22	0.0244	4.39	0.0448	5.000
1 10 100 1,000 10,000	0	0.0805	—	0.148	—	0.060	—	0.1410	—	0.0545	—	0.1362	—
	1	0.0873	1.0	0.161	1.0	0.0678	1.0	0.1585	1.0	0.0625	1.0	0.1570	1.0
	2	0.0953	2.176	0.1743	2.03	0.0770	2.79	0.1805	2.260	0.0713	2.10	0.1610	2.154
	3	0.1050	5.603	0.190	2.23	0.0867	3.715	0.1945	4.49	0.0817	2.40	—	—
	4	0.1172	5.397	0.214	5.08	0.1042	5.667	0.2600	6.80	0.0930	3.06	—	—
1 10 100 1,000 10,000	0	0.0710	—	0.1237	—	0.0327	—	0.0565	—	0.01340	—	0.0263	—
	1	0.0777	1.0	0.1330	1.0	0.0385	1.0	0.0650	1.0	0.01646	1.0	0.0313	1.0
	2	0.0827	1.745	0.1398	1.731	0.0431	1.793	0.0723	1.859	0.01920	1.895	0.0356	1.84
	3	0.0862	2.265	0.1448	2.269	0.0467	2.414	0.0787	2.612	0.02162	2.686	0.0395	2.24
	4	0.0888	2.660	0.1482	2.634	0.0497	2.931	0.0835	3.172	0.02370	3.366	0.0427	3.28
1 10 100 1,000 10,000	0	0.1218	—	0.325	—	0.0375	—	0.0892	—	0.0167	—	0.0387	—
	1	0.1415	1.0	0.382	1.0	0.0461	1.0	0.1090	1.0	0.0215	1.0	0.0475	1.0
	2	0.1582	1.746	0.422	1.701	0.0540	1.918	0.1280	1.91	0.0258	1.896	0.0553	1.886
	3	0.1675	2.320	—	—	0.0605	2.674	0.1440	2.68	0.0292	2.604	0.0630	2.761
	4	0.1765	2.775	—	—	0.0656	3.267	0.1580	3.44	0.0325	3.260	0.0702	3.576
1 10 100 1,000 10,000	0	0.1056	—	0.1960	—	0.0870	—	0.188	—	0.0870	—	0.188	—
	1	0.117	1.0	0.2160	1.0	0.1042	1.0	0.222	1.0	0.1045	1.0	0.226	1.0
	2	0.1267	1.763	0.2398	1.690	0.1200	1.92	0.248	1.76	0.1200	1.943	0.257	1.81
	3	0.1321	2.325	0.2410	2.250	0.1350	2.72	0.274	2.52	0.1360	2.743	—	—
	4	0.1364	2.702	0.2495	2.675	0.1483	3.48	0.298	3.23	0.1482	3.497	—	—
1 10 100 1,000 10,000	0	0.0710	—	0.1237	—	0.0327	—	0.0565	—	0.01340	—	0.0263	—
	1	0.0777	1.0	0.1330	1.0	0.0385	1.0	0.0650	1.0	0.01646	1.0	0.0313	1.0
	2	0.0827	1.745	0.1398	1.731	0.0431	1.793	0.0723	1.859	0.01920	1.895	0.0356	1.84
	3	0.0862	2.265	0.1448	2.269	0.0467	2.414	0.0787	2.612	0.02162	2.686	0.0395	2.24
	4	0.0888	2.660	0.1482	2.634	0.0497	2.931	0.0835	3.172	0.02370	3.366	0.0427	3.28
1 10 100 1,000 10,000	0	0.1218	—	0.325	—	0.0375	—	0.0892	—	0.0167	—	0.0387	—
	1	0.1415	1.0	0.382	1.0	0.0461	1.0	0.1090	1.0	0.0215	1.0	0.0475	1.0
	2	0.1582	1.746	0.422	1.701	0.0540	1.918	0.1280	1.91	0.0258	1.896	0.0553	1.886
	3	0.1675	2.320	—	—	0.0605	2.674	0.1440	2.68	0.0292	2.604	0.0630	2.761
	4	0.1765	2.775	—	—	0.0656	3.267	0.1580	3.44	0.0325	3.260	0.0702	3.576
1 10 100 1,000 10,000	0	0.1056	—	0.1960	—	0.0870	—	0.188	—	0.0870	—	0.188	—
	1	0.117	1.0	0.2160	1.0	0.1042	1.0	0.222	1.0	0.1045	1.0	0.226	1.0
	2	0.1267	1.763	0.2398	1.690	0.1200	1.92	0.248	1.76	0.1200	1.943	0.257	1.81
	3	0.1321	2.325	0.2410	2.250	0.1350	2.72	0.274	2.52	0.1360	2.743	—	—
	4	0.1364	2.702	0.2495	2.675	0.1483	3.48	0.298	3.23	0.1482	3.497	—	—
1 10 100 1,000 10,000	0	0.0710	—	0.1237	—	0.0327	—	0.0565	—	0.01340	—	0.0263	—
	1	0.0777	1.0	0.1330	1.0	0.0385	1.0	0.0650	1.0	0.01646	1.0	0.0313	1.0
	2	0.0827	1.745	0.1398	1.731	0.0431	1.793	0.0723	1.859	0.01920	1.895	0.0356	1.84
	3	0.0862	2.265	0.1448	2.269	0.0467	2.414	0.0787	2.612	0.02162	2.686	0.0395	2.24
	4	0.0888	2.660	0.1482	2.634	0.0497	2.931	0.0835	3.172	0.02370	3.366	0.0427	3.28
1 10 100 1,000 10,000	0	0.1218	—	0.325	—	0.0375	—	0.0892	—	0.0167	—	0.0387	—
	1	0.1415	1.0	0.382	1.0	0.0461	1.0	0.1090	1.0	0.0215	1.0	0.0475	1.0
	2	0.1582	1.746	0.422	1.701	0.0540	1.918	0.1280	1.91	0.0258	1.896	0.0553	1.886
	3	0.1675	2.320	—	—	0.0605	2.674	0.1440	2.68	0.0292	2.604	0.0630	2.761
	4	0.1765	2.775	—	—	0.0656	3.267	0.1580	3.44	0.0325	3.260	0.0702	3.576
1 10 100 1,000 10,000	0	0.1056	—	0.1960	—	0.0870	—	0.188	—	0.0870	—	0.188	—
	1	0.117	1.0	0.2160	1.0	0.1042	1.0	0.222	1.0	0.1045	1.0	0.226	1.0
	2	0.1267	1.763	0.2398	1.690	0.1200	1.92	0.248	1.76	0.1200	1.943	0.257	1.81
	3	0.1321	2.325	0.2410	2.250	0.1350	2.72	0.274	2.52	0.1360	2.743	—	—
	4	0.1364	2.702	0.2495	2.675	0.1483	3.48	0.298	3.23	0.1482	3.497	—	—
1 10 100 1,000 10,000	0	0.0710	—	0.1237	—	0.0327	—	0.0565	—	0.01340	—	0.0263	—
	1	0.0777	1.0	0.1330	1.0	0.0385	1.0	0.0650	1.0	0.01646	1.0	0.0313	1.0
	2	0.0827	1.745	0.1398	1.731	0.0431	1.793	0.0723	1.859	0.01920	1.895	0.0356	1.84
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	2	0.1582	1.746	0.422	1.701	0.0540	1.918	0.1280	1.91	0.0258	1.896	0.0553	1.886
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	4	0.1765	2.775	—	—	0.0656	3.267	0.1580	3.44	0.0325	3.260	0.0702	3.576
1 10 100 1,000 10,000	0	0.1056	—	0.1960	—	0.0870	—	0.188	—	0.0870	—	0.188	—
	1	0.117	1.0	0.2160	1.0	0.1042	1.0	0.222	1.0	0.1045	1.0	0.226	1.0
	2	0.1267	1.763	0.2398	1.690	0.1200	1.92	0.248	1.76	0.1200	1.943	0.257	1.81
	3	0.1321	2.325	0.2410	2.250	0.1350	2.72	0.274	2.52	0.1360	2.743	—	—
	4	0.1364	2.702	0.2495	2.675	0.1483	3.48	0.298	3.23	0.1482	3.497	—	—
1 10 100 1,000 10,000	0	0.0710	—	0.1237	—	0.0327	—	0.0565	—	0.01340	—	0.0263	—
	1	0.0777	1.0	0.1330	1.0	0.0385	1.0	0.0650	1.0	0.01646	1.0	0.0313	1.0
	2	0.0827	1.745	0.1398	1.731	0.0431	1.793	0.0723	1.859	0.01920	1.895	0.0356	1.84
	3	0.0862	2.265	0.1448	2.269	0.0467	2.414	0.0787	2.612	0.02162	2.686	0.0395	2.24
	4	0.0888	2.660	0.1482	2.634	0.0497	2.931	0.0835	3.172	0.02370	3.366	0.0427	3.28
1 10 100 1,000 10,000	0	0.1218	—	0.325	—	0.0375	—	0.0892	—	0.0167	—	0.0387	—
	1	0.1415	1.0	0.382	1.0	0.0461	1.0	0.1090	1.0	0.0215	1.0	0.0475	1.0
	2	0.1582	1.746	0.422	1.701	0.0540	1.918	0.1280	1.91	0.0258	1.896	0.0553	1.886
	3	0.1675	2.320	—	—	0.0605	2.674	0.1440	2.68	0.0292	2.604	0.0630	2.761
	4	0.1765	2.775	—	—	0.0656	3.267	0.1580	3.44	0.0325	3.260	0.0702	3.576
1 10 100 1,000 10,000	0	0.1056	—	0.1960	—	0.0870	—	0.188	—	0.0870	—	0.188	—
	1	0.117	1.0	0.2160	1.0	0.1042	1.0	0.222	1.0	0.1045	1.0	0.226	1.0
	2	0.1267	1.763	0.2398	1.690	0.1200	1.92	0.248	1.76	0.1200	1.943	0.257	1.81
	3	0.1321	2.325	0.2410	2.250	0.1350	2.72	0.274	2.52	0.1360	2.743	—	—
	4	0.1364	2.702	0.2495	2.675	0.1483	3.48	0.298	3.23	0.1482	3.497	—	—
1 10 100 1,000 10,000	0	0.0710	—	0.1237	—	0.0327	—	0.0565	—	0.01340	—	0.0263	—
	1	0.0777	1.0	0.1330	1.0	0.0385	1.0	0.0650	1.0	0.01646			

graph of $(Y_t - Y_1)/(Y_{10} - Y_1)$ against t (log scale) remains a straight line; for Neoprene, the shape of the curve is unchanged; for soft and medium Hycar the curve is modified slightly, as in Figure 2.

The influence of cure on relative creep can be seen by comparing Figures 6 and 7; an additional 20-minute curing time reduces the amount of creep slightly.

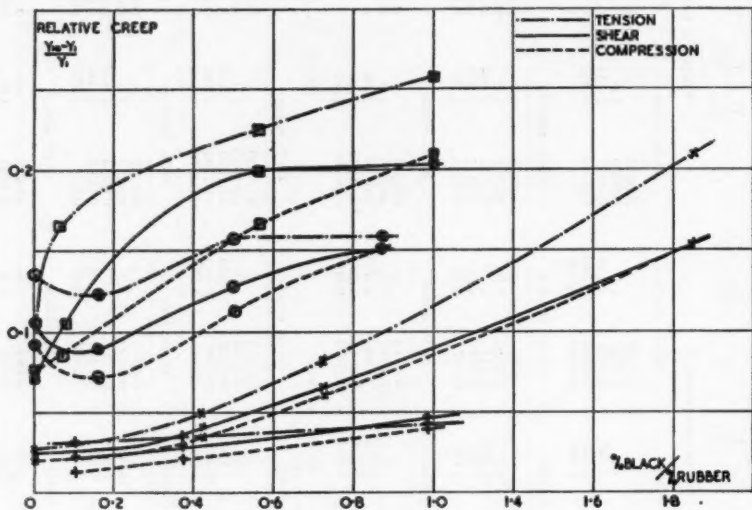


Fig. 6.—Relative creep vs. black for 20-minute cure.

Curve, 20 minutes at 153° C
 + Natural rubber, resilient
 × Natural rubber, bonding
 ○ Neoprene
 □ Hycar

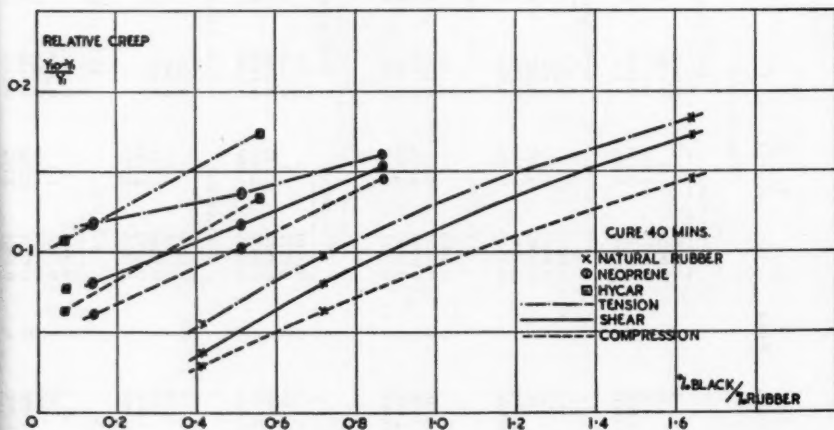


Fig. 7.—Relative creep vs. black for 40-minute cure.

Influence of carbon black.—For natural rubber, the creep remains proportional to $\log t$, whatever the percentage of carbon black. For Neoprene and Hycar, the influence of black is shown in Figure 2.

Figures 6 and 7 reveal to what degree relative creep is due to the presence of carbon black. It is unlikely that the addition of 3 per cent carbon black to Neoprene reduces primary creep; the drop in value at this point is probably due to variations in processing and conditions of storage.

There is for each polymer a lower limit to the creep attained by the gum stock and an upper limit approached with a black-rubber ratio of 0.6 in Neoprene.

It can now be seen from Tables II and III that, whereas the values of $(Y_{10} - Y_1)/Y_1$ depend on the geometry of loading and the load, the values of $(Y_1 - Y_1)/(Y_{10} - Y_1)$ are not.

Geometry of loading.—Relative creep in shear is less than in tension and more than in compression. Figures 3, 4, and 5, in which $(Y_{10} - Y_1)/H$ is plotted against Y_1/H and in which the relative creep $(Y_{10} - Y_1)/Y_1$ is represented by the slope of these lines, indicate that at the origin there is no gradual transition from creep in tension to creep in compression but an abrupt change. No simple relationship is arrived at, however, by plotting relative creep against the tensile or compressive stress calculated on the actual cross section.

STIFFNESS

The observation of deflection continuously over many minutes enables the 1-minute deflection to be very accurately assessed from the deflection-time curve, and Figures 8 to 11 show curves of load per unit of original area *vs.* 1-minute strain for all compounds in tension, compression, and shear.

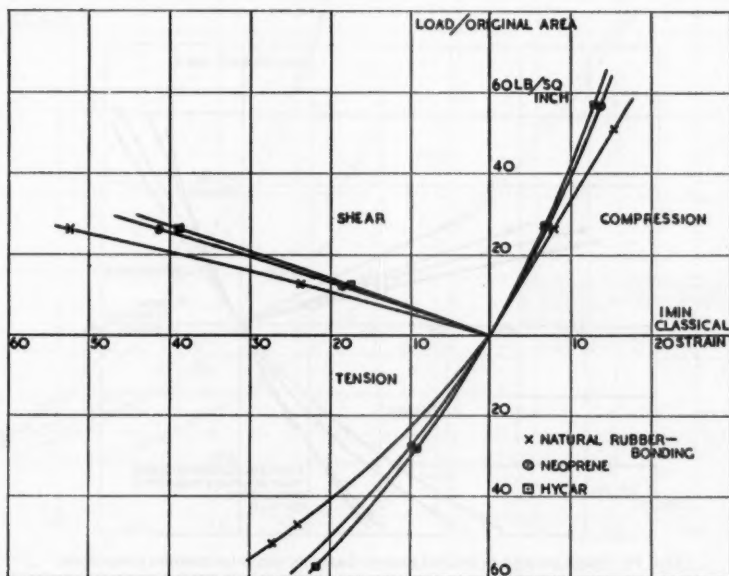


FIG. 8.—Load per unit of original area *vs.* 1-minute strain for gum stocks.

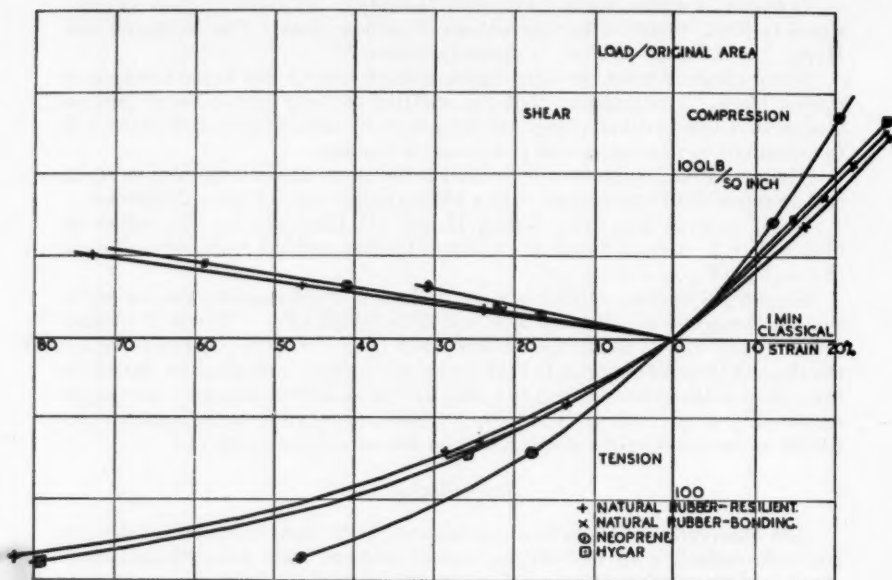


FIG. 9.—Load per unit of original area vs. 1-minute strain for soft compounds.

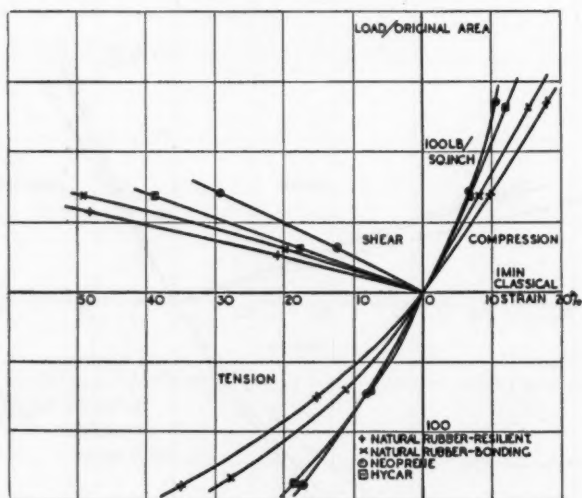


FIG. 10.—Load per unit of original area vs. 1-minute strain for medium compounds.

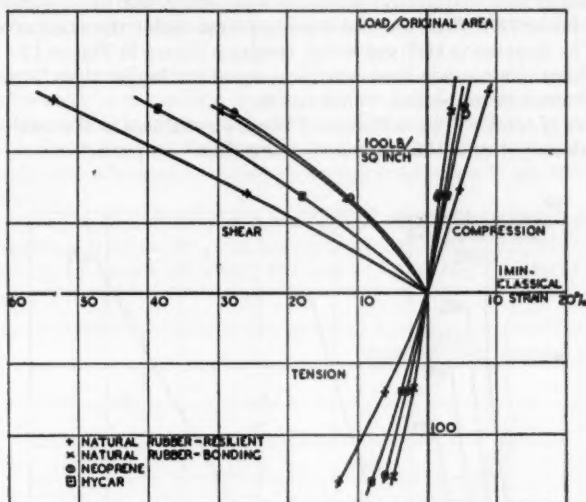


FIG. 11.—Load per unit of original area vs. 1-minute strain for hard compounds.

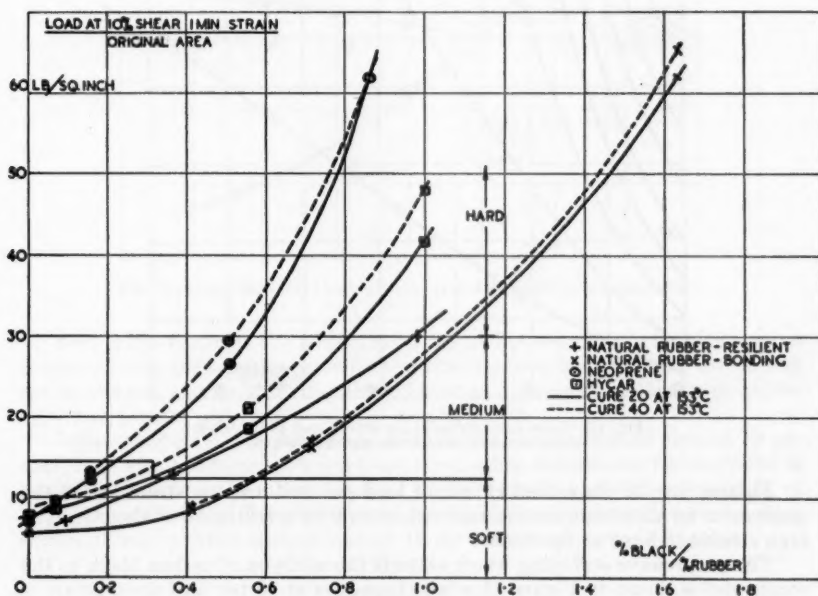


FIG. 12.—Load at 10 per cent shear, 1-minute strain per unit of original area vs. per cent black.

Influence of cure.—Certain specimens were subjected to an additional cure of 20 minutes at 153° C and tested a second time under the same conditions as before. The increase in stiffness which results is shown in Figure 12. Resilient natural rubber compounds have not been cured for longer than 20 minutes, as no improvement in properties would result.

Influence of black.—The influence of black on stiffness is of practical importance and already forms the subject of more than one paper⁴.

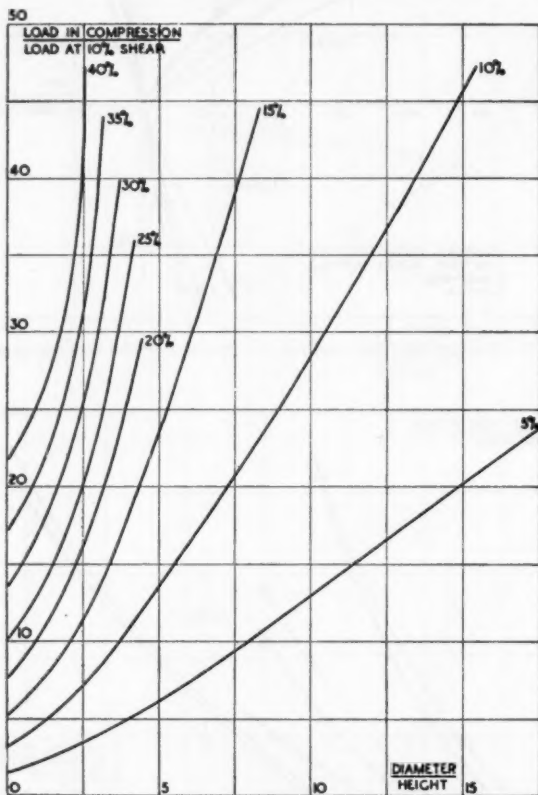


FIG. 13.—Load in compression per unit of load at 10 per cent shear strain vs. diameter-height of specimen.

Figures 8 to 11 show that curves of load per unit area vs. strain are of the same form for all compounds considered, except for a falling off of shear load at high strains in hard compounds.

The progressive stiffening which attends the addition of carbon black to the compound is shown in Figure 12, where load-area at 10 per cent shear strain is plotted against percentage black. The addition of equal quantities of two blacks was dictated by other conditions than the investigation of creep, namely, the need for information on commercial compounds. Figure 12 shows also

that a natural rubber compounded only with lampblack may be slightly harder than that compounded with an equal quantity of lampblack and gas black combined.

Influence of shape of specimen.—In addition to the standard test-specimens, some were molded in a medium natural rubber bonding compound with the same diameter, but reduced height, and tested in compression. Specimens up to 2 inches in diameter were also tested in compression on an automatic testing machine under conditions of load history as nearly as possible the same as those described above.

Values of load in compression as a multiple of load at 10 per cent shear strain have been deduced from the original curves of load *vs.* strain, and plotted against shape factor up to values for which the ratio of diameter to height equals 17 (Figure 13).

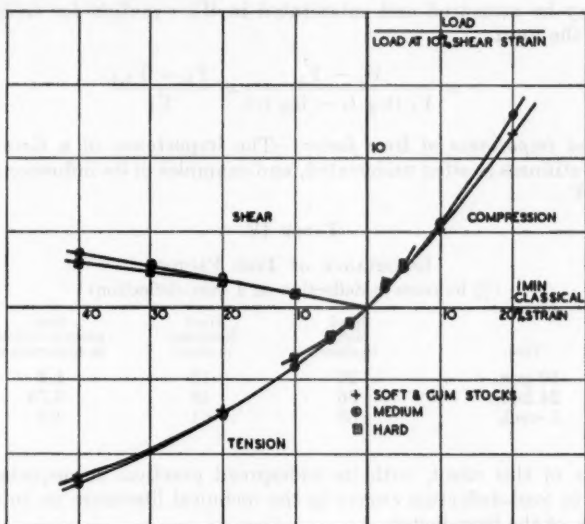


FIG. 14.—Load per unit of load at 10 per cent shear strain *vs.* 1-minute strain.

Zero shape factor is the condition in which the diameter is infinitely small compared with the height—one which can be obtained in practice by unbonding the specimens and compressing them between platens lubricated with castor oil. The platens and guides may be seen in Figure 1.

Influence of geometry of loading.—If load per unit of original area at 10 per cent shear strain is taken as a reference level, other stresses can be expressed in terms of it. Using the mean values of the gum stocks and soft compounds, of the four medium and four hard compounds, Figure 14 shows to what extent curves of load plotted against load at 10 per cent shear strain coincide.

SUMMARIZED DATA

From the designer's point of view the above results may be summarized as follows.

Given the compound, cure, and geometry of loading, the ratio of t -minute deflection to 1-minute deflection may be expanded:

$$\frac{Y_t}{Y_1} = \frac{Y_t - Y_1}{Y_{10} - Y_1} \times \frac{Y_{10} - Y_1}{Y_1} + 1$$

in which the first fraction may be read from Figure 2 and the second from Figures 6 and 7.

Given also the 1-minute strain, the corresponding ratio of load to area may be determined by referring to Figure 14 which gives the ratio of load at required strain to load at 10 per cent shear strain, and to Figure 12 which gives the load-area ratio at 10 per cent shear strain for all compounds.

If it is desired to obtain a value of the relative creep of a natural rubber compound in a test lasting 1 minute, values of Y corresponding to $t = 0.1$ and 1.0 minute may be measured and substituted in the equation for creep now rewritten in the form:

$$r = \frac{Y_t - Y_1}{Y_1 (\log t_2 - \log t_1)} = \frac{Y_1 - Y_{0.1}}{Y_1}$$

Practical importance of time factor.—The importance of a time factor in measuring stiffness is often underrated, and examples of its influence are shown in Table IV.

TABLE IV
IMPORTANCE OF TIME FACTOR
(% increase in deflection on 1 min.-deflection)

Time	Hard Hycar in shear	Hard Neoprene in shear	Soft natural rubber in compression
10 min.	20	15	1.2
24 hours	56	48	3.78
1 week	68	61	4.8

In spite of this effect, with its widespread practical consequences, many references to load-deflection curves in the technical literature on rubber make no mention of the time factor.

CONCLUSIONS

The addition of two compounded blacks renders induction concerning the mechanism of either black uncertain. Generally speaking, however, the black in a specimen of given size may be thought of as replacing its volume of rubber, so, when under a particular load, the rubber remaining is more highly stressed. Because the rubber is highly stressed, the relative creep is increased, but because there is less of it, the actual creep is diminished.

For a given shape of specimen, all soft compounds and gum stocks have the same curve of load-area *vs.* strain up to 20 per cent compression, 40 per cent tension, and 40 per cent shear; the same applies to medium hard stocks. The stiffness of any such specimen can be expressed in terms of a convenient reference level, such as the load-area at 10 per cent shear 1-minute strain.

Over a wide range of conditions in which polymer, compound, cure, and geometry of loading have been varied, 10-minute creep remains proportional to 1-minute deflection for each particular geometry of loading, but in tension

the ratio of 10-minute creep to 1-minute deflection is greater than in shear, in compression less—an effect which is generally more marked in soft than in hard compounds.

Measurements of creep on specimens in which the ratio of diameter to height is greater than 1.6 were, mainly on account of the small deflections involved, not sufficiently accurate to be included. It is reasonable to assume, however, that creep is proportional to strain under other conditions than those considered here, such as in specimens of other shapes and specimens loaded in bending and torsion.

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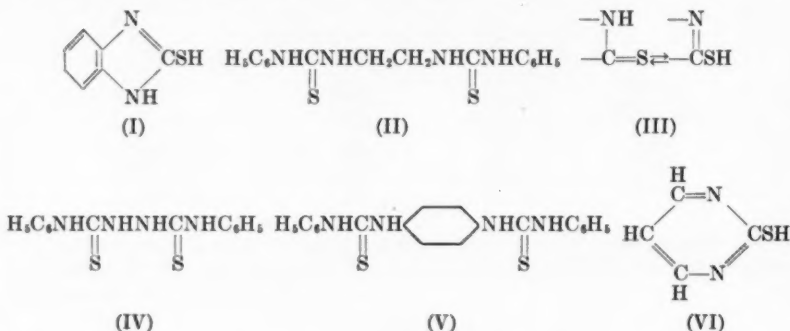
- ¹ Leaderman, "Elastic and creep properties of filamentous materials and other high polymers", Textile Foundation of Washington, 1943.
- ² Mullins, *J. Rubber Research* **16**, 275 (1947).
- ³ Jenkins and Cooper, *Proc. 2nd Rubber Technol. Conf. London*, 1948, p. 214.
- ⁴ Gehman, *Ind. Eng. Chem.* **36**, 715 (1944).

THE CHEMICAL STRUCTURE RESPONSIBLE FOR THE DEACTIVATING EFFECT OF COMPOUNDS WHICH PROTECT RUBBER FROM DETERIORATION BY OXYGEN *

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One of the present authors has already offered evidence which indicates the existence of a deactivating effect, whereby vulcanized rubber is protected against deterioration by oxygen¹. This effect is evident with such compounds as mercaptobenzimidazole (I), mercaptobenzoxazole, and ethylene-bis(*N,N'*-phenylthiourea) (II), and the phenomenon seems to be connected in some way with the presence in the molecule of a thiol group united to a nitrogen atom under such conditions that the possible tautomerism between the thion and thiol forms (III) is probably displaced toward the thiol form².



We have completed these earlier experiments by a more systematic study, which has included an examination of the influence of cyclization, the nature of the ring, and hetero atoms.

Among aliphatic compounds, thiourea shows a rather marked deactivating effect, monophenylthiourea a smaller effect, and *N,N'*-diphenylthiourea none at all. Consequently substitution at the nitrogen atoms probably orients the structure toward the thion form, and independently of this, the nature of such substitution influences the displacement of the equilibrium, since bis(*N*-phenylthiocarbamoyl)hydrazine (IV) and ethylene-bis(*N,N'*-phenylthiourea) are deactivating agents, whereas *p*-phenylene-bis(*N,N'*-phenylthiourea) (V) and *m*-phenylene-bis(*N,N'*-phenylthiourea) are practically inactive. Among the thio acids tested, which included monothiobenzoic acid, dithiobenzoic acid, and

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 231, pages 145-147, July 10, 1950. The title of this translation is amplified so as to be more explicit. The original title is "Sur la Structure Chimique Entraînant l'Effet Désactivateur".

ethylxanthic acid, only the first of these showed even a weak deactivating effect. This seems to indicate that structures of this character are not favorable to such action. On the contrary, when the carbon atom carrying the sulfur is united to an unsubstituted nitrogen atom, as in dithiocarbamic acid (or thiolthioncarbamie acid), the deactivating power is well defined. This acid can also be regarded as a thioamide, and other thioamides which were tested, viz., thiobenzamide and dithiooxamide, likewise gave good results.

Since the pentatomic ring of mercaptobenzimidazole and of mercaptoimidazole² was found to have such a favorable effect, further tests were carried out to ascertain whether a hexatomic structure would likewise give positive results. Various derivatives of 2-mercaptopyridine (VI) were tested, including 2-mercapto-4,6-dimethylpyrimidine, 2-mercapto-4,6-dihydroxypyrimidine, and 2,4,6-trimercaptopyrimidine. Each of these compounds showed a deactivating effect, but to a much less degree than that of the derivatives containing a pentatomic ring.

It has been seen that, in the cyclic series, the deactivating effect is evident with compounds in the structures of which the carbon atom carrying a thiol group is located either between two nitrogen atoms or between a nitrogen atom and an oxygen atom. If, now, we turn to compounds having structures such as those of 2-mercaptopyridine, thiophenol, and β -thionaphthol, we find that they have practically no protective action.

In conclusion, it may be said that, whereas various aliphatic compounds definitely do have deactivating effects, they show in general less protective action than do cyclic deactivating agents. Consequently, even if the cyclic structure is not indispensable, it certainly enhances the deactivating effect. With respect to the character of the ring, it should preferably be pentatomic. The most effective structure is, then, one in which the carbon atom carrying a thiol group is situated between two nitrogen atoms or between a nitrogen atom and an oxygen atom.

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- ² Le Bras and Hildenbrand, *Compt. rend.* 223, 724 (1946); *RUBBER CHEM. & TECHNOL.* 20, 427 (1947).

100 parts of monomers with 100 parts of methyleyclohexane as diluent. The inherent viscosity was 3.4, the gel content 3 per cent, and the Mooney (large rotor) viscosity 61.

The solvents were purified before use. Carbon tetrachloride was treated with acidified potassium permanganate, washed with water, dried over calcium chloride, and distilled before use. Reagent grade acetone was dried and distilled. Reagent grade butanol was distilled over dried potassium carbonate.

Each polymer was purified before oxidation. It was dissolved in chloroform, filtered to remove gel, if any, and precipitated with methanol containing 1 per cent phenyl-2-naphthylamine antioxidant. This procedure was repeated three times. The polymers were not dried after reprecipitation, but immediately put in chloroform to be dissolved again. No additional gel formed after the initial gel had been removed. After the last precipitation the polymer was vacuum-dried for 8 hours at 50° C.

The oxidation was carried out in 16-ounce narrow-mouth screw-cap bottles. The bottle caps were lined with polyethylene. Eighty milliliters of carbon tetrachloride and 0.5000 gram of the purified polymer were placed in the bottle and rolled overnight to dissolve the rubber. A solution of 4.10 grams of potassium permanganate (100 per cent) in 150 cc. of distilled water was added, followed by 1.27 grams of sulfuric acid (100 per cent), in the form of a standardized 2 *N* solution. Enough water was then added to make a total volume of 400 cc. The bottle was placed in a 30° C water bath and tumbled overnight. On removal from the bath, the bottle was placed in an ice-salt mixture for 30 minutes and opened, and the carbon dioxide content was determined as follows. Nitrogen was bubbled through the oxidized mixture for 4 hours to displace the carbon dioxide, which was collected in two towers connected in series, each containing 175 cc. of standardized 0.5 *N* potassium hydroxide.

After removal of carbon dioxide, the mixture was neutralized with standardized 0.5 *N* sodium hydroxide to the phenolphthalein end point. The hydrated manganese dioxide was filtered off, washed thoroughly with hot water, then digested for 1 hour with boiling water, filtered, and dried for 16 hours at 70° C. A manganese analysis showed the residue to be the hydrated manganese dioxide, $\text{MnO}_2 \cdot \text{H}_2\text{O}$, rather than MnO_2 . The washings were saved. The filtrate from the manganese dioxide filtration consisted of a water layer and a carbon tetrachloride layer. The organic layer was separated and washed three times with water, and the washings were added to the water layer. The organic layer was then checked for solids content. At this point, if necessary, additional sodium hydroxide was added to the water layer to maintain it alkaline to the phenolphthalein end point. The solution was then evaporated to dryness on the steam bath. The residue was treated with standardized 3 *N* hydrochloric acid to a pH of 2.5. Acetone was added until a precipitate was no longer obtained. After the inorganic salts had been filtered off, the aqueous acetone solution was dried with anhydrous magnesium sulfate. When the dried solution was evaporated to dryness, it was necessary to extract with dry acetone to isolate the organic acids, as the residue still contained inorganic salts. The acid mixtures obtained were soft and greasy to the touch.

A separate experiment was run with the 50° emulsion polymer, to determine if any volatile acids were formed.

After oxidation in the usual manner, the hydrated manganese dioxide residue was filtered off and washed. The filtrate and washings were combined and the water and carbon tetrachloride layers were separated. The organic layer was washed twice with water and the washings were added to the water layer. No acid was found when the organic layer was titrated with standard

TABLE I
PERMANGANATE OXIDATION OF BUTADIENE POLYMERS

Polymer	Acids formed (equiv.)	CCl ₄ residue (g.)	Solid acids (g.)	Solid acids ^a (%) theor.)	CO ₂ (g.)	Side vinyl ^b groups (%)
Emulsion (50° C)	0.0336	0.0739	1.2490	62.2	0.2209	18.0
Emulsion (-10° C)	0.0336	0.0706	1.3155	65.4	0.2036	16.5
Sodium	0.0267	0.0858	0.9315	46.3	0.3815	59 ^c
Alfin	0.0333	0.1636	1.2748	63.4	0.2599	27.5 ^d

All weights given on basis of 1 gram of polymer oxidized.

^a Theoretical value taken as 2.01 grams.

^b Values obtained by reaction with perbenzoic acid.

^c Value obtained by Kolthoff, Lee, and Mair¹¹.

^d Value obtained by D'Ianni, Naples, and Field¹².

alkali. The water layer was then vacuum-distilled through a short packed column, and the distillate was collected in two receivers, one packed in a salt-ice mixture, the other in a dry ice-acetone bath. The water was distilled in a water bath at 50° to 60° C until 75 to 100 cc. remained in the distillation flask. The distillates in the traps were combined, and aliquot portions were titrated for acid content with 0.02 *N* sodium hydroxide. Only a negligible amount of volatile acids were found, 0.00002 equivalent per gram of rubber oxidized.

Table I summarizes the data on the oxidation of the various polymers studied. The emulsion and Alfin polymers yielded approximately the same equivalents of solid acids, whereas the sodium polymer produced substantially less. The residue in the carbon tetrachloride layer amounted to 7 to 16 per cent of the original weight of the polymer, and represents that portion of the polymer which was insufficiently oxidized to be soluble in a sodium hydroxide solution. The emulsion and Alfin polymers yielded about 60 to 65 per cent of the theoretical amount of solid acids, whereas the amount from the sodium polymer was less, as was expected because it contains a much larger amount of side vinyl groups which were oxidized to carbon dioxide. The amounts of carbon dioxide formed during the oxidation correlated well with the side vinyl contents, as determined independently by perbenzoic acid titration.

PARTITION CHROMATOGRAPHIC ANALYSIS

The oxidation products were separated and analyzed by the excellent partition chromatographic technique developed by Marvel and Rands⁹ for the analysis of products of ozonolysis of synthetic polymers. The column of silicic acid was similar to the one described by Marvel and Light¹³, except that glycerol was not used and the composition of the eluant was changed slightly. This eluant resulted in a better separation than the one in which each fraction was 100 cc.

COMPOSITION OF ELUANT

Ethyl alcohol (absolute) (%)	Chloroform (%)	Total volume (cc.)
0	100	50
5	95	100
10	90	150
15	85	150
20	80	100
25	74	100
30	70	100

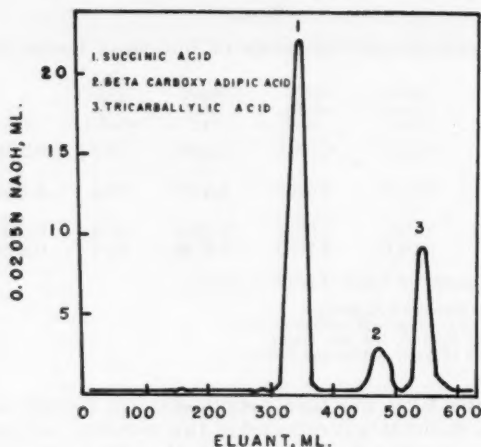


Fig. 1.—Chromatogram of known mixture of acids.

For titration with standard alkali, 250-cc. glass-stoppered Erlenmeyer flasks were used, because vigorous shaking was required for complete neutralization.

When a chloroform-butanol mixture⁹ was the eluant, there was no essential difference in the general appearance of the chromatograms, although there was a better separation of the acids from the sodium polymer oxidation products. The operation time with the chloroform-butanol eluant is slower than with the chloroform-ethyl alcohol eluant (12 hours *vs.* 8 hours).

CHROMATOGRAMS OF KNOWN ACID MIXTURES

To determine the peak volume for each acid, a chromatogram was developed of a known mixture of succinic, β -carboxyadipic, and tricarballic acids, as shown in Figure 1. This chromatogram established the relative positions of the acids for use in comparing with an unknown, when developed under the same conditions:

Band no.	Known acids (peak volume)	Unknown acids (peak volume)
1	360 Succinic	350
2	490 β -Carboxyadipic	490
3	560 Tricarballic	560

The unknown was the acid mixture obtained from the 50° C emulsion polybutadiene. This comparison indicates that the three major peaks are due to the acids represented above. In some runs, because of the conditions of the experiment, the peaks may shift to the right or to the left. The two chromatograms above were developed in succession. In the other chromatograms shown the peaks have shifted to the left.

IDENTIFICATION OF ACIDS FROM OXIDATION PRODUCTS

To confirm the existence of the three acids mentioned, some of the same acid mixture from the 50° C emulsion polymer was passed through a large chromato-

graphic column and the acids were separated. Except for the size, the construction and preparation of this column were similar to those of the smaller column. The length of the tube was 75 cm., and the inside diameter was 48 mm. The column was prepared by mixing 85 cc. of distilled water with 213 grams of silicic acid. After the eluant was added, it was forced through the column and collected in 100-cc. fractions. A 10-cc. aliquot of this was titrated, the remainder being saved to isolate the pure acid.

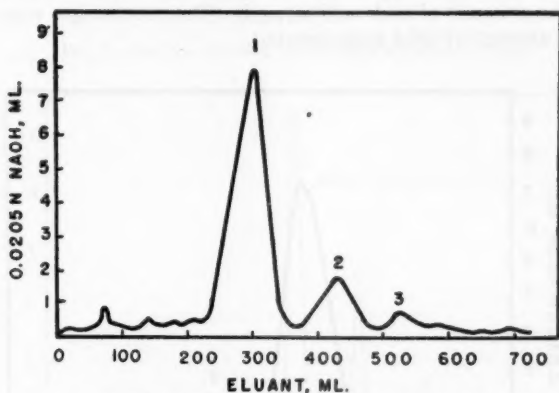


Fig. 2.—Analysis of 50° C emulsion polybutadiene oxidation products.

The eluant was the same as used for the smaller column, except that 8 times the volume was used for each charge of eluant.

The mixture (2.2 grams) of acids was dissolved in 15 cc. of absolute ethyl alcohol and 6 cc. of chloroform and added to the column. The chromatogram was similar to that shown in Figure 2, the major peaks being 1, 2, and 3. The solvent from these fractions was allowed to evaporate at room temperature. The residues were purified by dissolving in a minimum amount of acetone and adding chloroform until precipitation was complete. The products were separated by filtration and dried. Melting point and mixed melting point determinations with known acids gave the following results:

	° C
1. Melting point of acid from band 1	185–186
Melting point of authentic succinic acid	185–186
Mixed melting point	185–186
2. Melting point of acid from band 2	119
Melting point of authentic β -carboxyadipic acid	119
Mixed melting point	119
3. Melting point of acid from band 3	150
Melting point of authentic tricarballic acid	154–157
Mixed melting point	152

Because the melting point of the acid from band 3 was lower than for the authentic sample of tricarballic acid, additional work was done to confirm its identity. A small amount of pure tricarballic acid was added to the mixture and the chromatogram was developed again. The peak of band 3 was accentuated in proportion to the amount of pure acid added.

ANALYSIS OF CHROMATOGRAMS

The results of the partition chromatographic analysis of the oxidation products of the various polymers are illustrated in Figures 2, 3, 4, and 5, and summarized in Table II. Figure 6 represents the analysis of the products from sodium polybutadiene with a chloroform-butanol eluant, whereas all other analyses illustrated were carried out with a chloroform-ethyl alcohol eluant. By measuring the areas under each of the peaks, quantitative figures were obtained for the amounts of each acid formed. The percentages were calculated on the total amount of solid acids isolated.

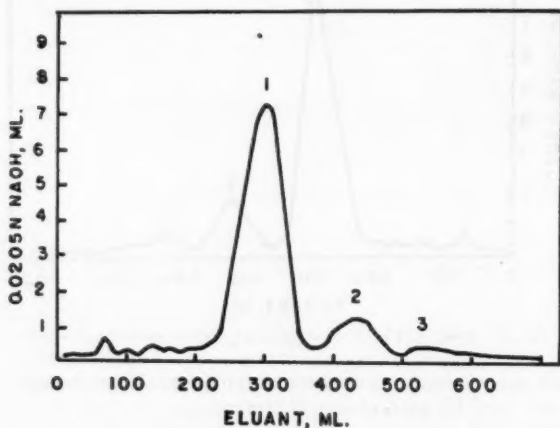


FIG. 3.—Analysis of -10°C emulsion polybutadiene oxidation products.

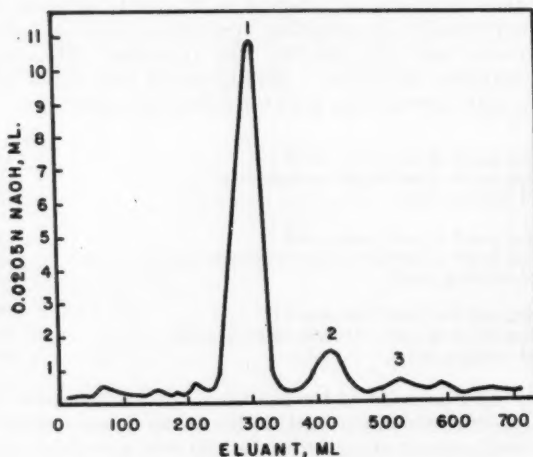


FIG. 4.—Analysis of Alfin polybutadiene oxidation products.

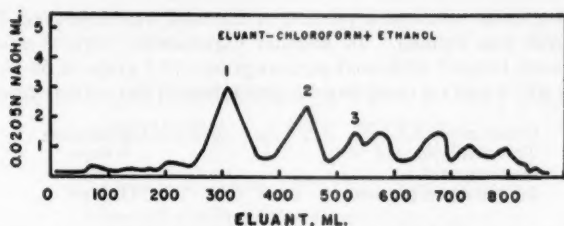


FIG. 5.—Analysis of sodium polybutadiene oxidation products.

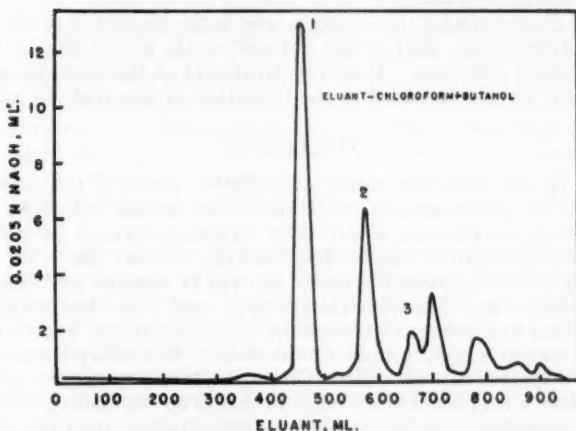


FIG. 6.—Analysis of sodium polybutadiene oxidation products. Chloroform-butanol eluent.

TABLE II

OXIDATION PRODUCTS BY CHROMATOGRAPHIC ANALYSIS

Polymer	Succinic acid (%)	β -Carboxyadipic acid (%)	Tricarballic acid (%)
Emulsion (50° C)	57.4	11.5	3.0
Emulsion (-10° C)	62.6	10.3	1.8
Sodium	20.8	15.1	6.6
Alfin	56.6	9.0	3.0

ORIGIN OF TRICARBALLYLIC ACID

Tricarballic acid is believed to arise from the oxidation of the structure formed by the saturation with butadiene of the allylic radical from two 1,4-addition units. However, Marvel¹⁴ has also suggested that in ozonolysis reactions it may be formed by a secondary rather than primary oxidation process. Because this possibility also exists in permanganate oxidations, experiments were devised to obtain additional information.

One possibility is the oxidation of β -carboxyadipic acid to tricarballic acid. However, when a purified sample of β -carboxyadipic acid was treated with

acidic permanganate solution, a portion of the acid was destroyed, but no tricarballic acid was formed. In another experiment, various acids (0.0085 equivalent) were treated with acid permanganate (0.2 gram in 50 cc. of water) and the time was noted for complete decolorization of the permanganate:

Oxalic acid	10 minutes
Tricarballic acid	6 days
Succinic acid	11 days
β -Carboxyadipic acid	11 days

It seems unlikely that β -carboxyadipic acid is the precursor of tricarballic acid, and the strong possibility therefore exists that the latter is the result of a primary oxidation product.

Marvel¹⁴ did not obtain tricarballic acid in the ozonolysis of the same 50° emulsion polybutadiene used in the authors' work, nor of similar Alfin and sodium butadiene polymers. However, treatment of the ozonides with 6 per cent hydrogen peroxide resulted in the formation of tricarballic acid.

CONCLUSION

In view of the failure to obtain quantitative yields of the expected carboxylic acids by permanganate oxidation of the several butadiene polymers studied, definite conclusions about their structures cannot be made. The results have a qualitative significance, however, in that the -10° emulsion polymer was found to produce a larger amount of succinic acid than the 50° emulsion polymer and less tricarballic acid, and thus they correlate with general thinking that lowered temperature of polymerization results in a polymer of more regular structure and less branching. The Alfin polymer, although prepared in a system entirely different from the emulsion system, gave results which indicated a microstructure similar to that of 50° emulsion polybutadiene. Sodium polybutadiene was less completely characterized than the others, but the large amounts of carbon dioxide and β -carboxyadipic acid isolated correlated well with the high percentage of external double bonds known to be present from other methods of analysis.

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DIRECT REINFORCEMENT OF NATURAL RUBBER LATEX MIXES *

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The advantages of the direct use of latex are well recognized because of the simplicity and economy of the practical techniques as well as the mechanical properties of the articles obtained. Because the rubber has not been submitted to mastication, it retains its intrinsic qualities unimpaired. Yet the use of latex has until now been limited to a relatively small number of applications, because it does not permit the fabrication of articles combining medium or high moduli and a hardness greater than 45 (Shore) with sufficiently great tensile strength and resistance to abrasion or to tearing. Loading materials can be added to latex, but reinforcing agents, which have such interesting effects on the properties of masticated rubber, do not exercise similar action in the case of latex.

The reinforcement of latex is a problem which has often attracted the attention of investigators, in view of its great interest from both the theoretical and practical points of view. However, little progress was achieved in this field previous to the authors' work¹ which, has led, apparently for the first time, to a solution of the reinforcement problem.

There is room for a precise definition of the term "direct reinforcement of mixes of latex", or, more briefly, "reinforcement of latex". This term should be interpreted to mean an improvement of the intrinsic properties of rubber obtained by the addition to a latex compound of a product or composition with "reinforcing" character, the final article being obtained without recourse to mixing on a mill at any time during its manufacture.

For historical interest only, reference is made to work dealing with the introduction of loading materials into latex for the purpose of assuring their perfect dispersion before coagulation and mastication. These experiments have had to do with the usual loading materials, such as carbon black, zinc oxide, and calcium carbonate², or more special products, such as Marbon resins³ and Indulin⁴. Numerous experiments were carried out, involving addition of resins, either by direct introduction of dispersions or by formation of the resins in the body of the latex. The operation was always followed by coagulation and thereafter mastication—for example, experiments with phenol-formaldehyde resins at various stages of condensation⁵, alkylated resins⁶, glyptal resins⁷, resins from condensation of fatty acids or their esters with maleic anhydride⁸, and polymers of acrylonitrile, acrylic esters, and styrene⁹.

Attempts to reinforce latex by the incorporation of mineral loading materials in the form of stabilized dispersions have not been successful. A certain increase of the modulus, hardness, and sometimes tear resistance is observed¹⁰, but the mechanical properties diminish rapidly. The expectations of van Rossem¹¹ on bentonite have not been confirmed¹².

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 381-386, February 1951. This paper was presented before the Rubber Division of the American Chemical Society at its International Meeting in Cleveland, Ohio, October 11-13, 1950.

Pliolite latex 190, a copolymer of styrene and butadiene, possesses good reinforcing qualities in the case of synthetic rubber latices¹³, but its effect on natural rubber latex is negligible. This also seems to be the case with colloidal silica¹⁴.

Twiss, Neale, and Hale¹⁵ experimented with the preparation of rubber mixes, reinforced by formation of the components of the mix in the body of the latex. Although their initial purpose was to obtain a coagulum designed to be milled thereafter, they nonetheless made certain useful observations on the compatibility of resins and latex. According to these authors, "it is possible by effecting the condensation of a polyhydroxyphenol, such as resorcinol, quinol, or pyrogallol, with formaldehyde in the presence of an alkaline solution as catalyst, to carry the resin formation further without separation of the resin. The solution of soluble resin can be mixed uniformly with latex, causing thickening of the latter; evaporation of a layer of the mixture causes further condensation or polymerization of the resin constituents and yields a uniform sheet of leatherlike consistency". This may indicate a certain degree of reinforcement, but Twiss and his coworkers have not pursued their investigations in that direction. They give no numerical data, and conclude that "none of the experiments provides a satisfactory solution to the problem of compounding natural rubber by the formation of the compounding ingredients in situ. The potential importance of the problem, however, is evident and each experiment in the desired direction, even if disappointing in itself, enables subsequent attempts to be made with more definite control of favorable factors and with an increased prospect of success".

The present authors have studied, in a detailed and systematic manner, the addition of resins at various stages of condensation, using a thermosensitive latex which permits the easy fabrication of objects by molding. Their aim in this study was to reconcile the conditions of drying and vulcanization of the gel with those of the condensation of the resin. They thus established that, by judicious regulation of the different factors, it was possible to attain reinforcement; in particular, certain soluble resorcinol-formaldehyde resins, condensed in alkaline medium, confer exceptional mechanical properties on vulcanizates of natural latex, surpassing those of the best mixtures of masticated rubber based on reinforcing blacks.

DETERMINATION OF CONDITIONS OF REINFORCEMENT

Experimental technique.—The latex (60 per cent solids) was prepared for molding by a thermosensitization treatment before addition of the vulcanization ingredients or other additives. The procedure employed depended on the action of trypsin¹⁶. The latex was treated with 0.5 to 2.0 per cent of powdered swine pancreas, which was diluted at first with 10 parts by weight of water. In general, this was done at room temperatures.

The thermosensitization, in the presence of the same quantity of zinc oxide and for the same temperature of gelation, is then a function of the amount of pancreas powder added, the temperature, and the time of reaction.

To obtain samples, the thermosensitive latex was mixed with the necessary ingredients for ultimate vulcanization, and with variable quantities of the loading materials being investigated. The ingredients were added in the form of aqueous dispersions to avoid coagulation of the latex and to obtain a homogeneous mixture.

The basic mixture, control mixture M, corresponded to the formula (parts by weight):

Dry rubber	100
Sulfur	2
Zinc oxide	3
Zinc diethyldithiocarbamate	1

After drying, it was vulcanized for 1 hour in the oven at 100° C.

Gelation was carried out in a metallic mold in hot water; then, after drying, the sheet was vulcanized at optimum conditions. Finally, the various properties were systematically determined by means of appropriate tests on the vulcanizates.

The loadings were appropriately incorporated in the form of dispersions or solutions, depending on the nature of the loading material (solid or liquid). It was usually necessary to stabilize the dispersions or solutions against coagulation and make them compatible with the heat-sensitized latex.

The nature and properties of the loading materials being investigated are very different and, in each case, it was necessary to determine the conditions of compatibility with the latex.

Incorporation of dispersed fillers.—On examination it was found that organic or inorganic loadings function differently according to their physical state.

Organic or inorganic loadings which exist as insoluble powders and are added to the latex in the form of dispersions act as inert fillers in masticated rubber. The stiffening of the mix, which increases with the quantity of filler incorporated, is accompanied by a decrease of the mechanical properties.

Organic fillers in soluble form or in colloidal suspension behave differently; stiffening of the mixture is always observed, but the mechanical properties are not altered as long as the concentration of the filler in the rubber does not exceed a certain variable, critical limit on the order of 10 to 25 per cent. In addition, there is generally an increase in tear resistance. This was observed, for example, with the urea-formaldehyde active resin 24562 (Société Nobel Française) or Pliolite Latex Type 190.

Therefore, in spite of the numerous tests performed and all the attention given to operating conditions, the results did not serve the purpose of the authors.

Formation in situ of synthetic resins.—Introduction of elementary components.—For satisfactory operation of the test, the components should not coagulate nor flocculate the latex at the time of incorporation; should mix easily with the latex and form a homogeneous medium; should not hinder gelation, and should not inhibit vulcanization.

The most encouraging results were obtained with vinyl resins, aminoplasts, and, above all, phenoplasts. Among the phenoplasts, the resorcinol-formaldehyde resins were noteworthy.

Nevertheless, the direct introduction into the thermosensitive latex of the resin, formaldehyde, and alkaline catalyst proved impossible for three reasons:

(1) instantaneous destabilization of the ammoniated latex, followed by its coagulation if there is an excess of aldehyde;

(2) The impossibility of the formation of the resin if there is an excess of ammonia, and

(3) The impossibility of gelation if there is an excess of alkaline catalyst or a stabilizer is present.

Attempts were made, therefore, to introduce the aldehyde in a less active form. Trioxymethylene may be used; its addition to the latex mix does not cause abrupt coagulation.

It is thus possible to obtain a certain reinforcement, as is shown in Table I, which shows the principal characteristics of the vulcanizates corresponding to the latex mix and of the same latex in which has been incorporated 13 per cent by weight of a preparation comprising 3 parts of resorcinol, 3 parts of trioxymethylene, 1 part of 15 per cent sodium hydroxide, and 6 parts of water.

There is a distinct increase in hardness and modulus, and a substantial improvement in resistance to abrasion and tear, as well as a certain increase in tensile strength. But the stability of this latex mix is still insufficient to allow practical application. Nevertheless, these results encouraged the authors to undertake a study of the incorporation of intermediate products of resinification, which might lead to further improvement.

Introduction of intermediate resinification products.—Here again the authors have examined a number of types of resins, principally aminoplasts and phenoplasts. However, the present communication discusses only resorcinol-formaldehyde resins, which gave the best results.

TABLE I
CHARACTERISTICS OF LATEX VULCANIZATES

	Latex	"Reinforced" latex
Tensile at break, kg./sq. cm.	330	355
Modulus at 300%, kg./sq. cm.	15	90
Elongation at break, %	750	675
Abrasion resistance, cc./hp./hour	600	350
Shore hardness	42	72
Resistance to tear, kg./cm.	50	85

Because the literature contains but little concerning the formation of these resins, the present authors conducted a detailed study of the resorcinol-formaldehyde condensation reaction in aqueous medium at high concentrations. [Soon after this work had been completed, several analogous studies were published, notably by Little and Pepper¹⁷, in which are found certain results which agree with those of the present authors.] We were thus able to determine the influence of various important factors such as concentration, pH, catalysts, temperature and time of condensation, molecular ratio of reactants, and exothermic character of the reaction, as well as the limits of operating conditions between which a single homogeneous liquid phase perfectly miscible with water is obtained.

For a resin to be compatible with vulcanizable latex thermosensitized by trypsin, it was necessary that the resin: (1) be present in the form of a liquid with sufficiently reduced viscosity; (2) be of proper concentration; (3) be free of uncombined formaldehyde; (4) have a pH which does not prevent the formation of the sensitizing zinc-ammonium ion; and (5) not have an unfavorable effect on the vulcanizing system of the latex mix.

The experimental conditions were chosen to comply with these requirements. If suitably condensed soluble resins were incorporated in thermosensitive latex, the gelation of the resulting mix could be controlled. Under these conditions the formaldehyde is totally combined with the resorcinol at the moment of introduction of the resin. The ammonia of the latex does not then

have a tendency to react and continues to fulfill its dual functions of preserving the latex during the period of manipulation and contributing to the formation of zinc-ammonium sensitizers.

INFLUENCE OF RESORCINOL-FORMALDEHYDE RESINS ON REINFORCEMENT

Operating conditions.—After preparation of the resin, it was mixed with the dispersion of the vulcanization ingredients and added to 60 per cent latex, previously treated with trypsin.

This dispersion had the following composition, and was added in the ratio of 10 parts per 100 parts of 60 per cent latex (parts by weight):

Zinc oxide	300
Sulfur	200
Zinc diethyldithiocarbamate	100
Dispergine CB at 20%	30
Gum tragacanth at 4%	140
Distilled water	890

This mix was poured into a metal mold, whereby slabs were obtained. The slabs most frequently used had a thickness after drying of about 2 mm. The mold was placed for 10 minutes in 70° C water to effect gelation. The samples were dried for 2 days in ambient air and 2 days in an oven at 40° C; then they were vulcanized by heating for 1 hour at 100° C in hot air.

The stability of the latex-resin mixture varies, according to the nature of the latex and the state of the resin, between 30 minutes and several hours. The delay is sufficient to permit casting in molds under satisfactory conditions.

On the other hand, gelation is more rapid in the presence of resin; the gels are finer and more coherent than in the case of latex alone and can be manipulated easily without deformation.

From the vulcanized sheets finally obtained, specimens were cut for mechanical tests. For the determination of modulus, tensile strength, and elongation at break, dumbbell test-pieces (Type I.F.C.), 2 mm. thick, with a constricted area 2 mm. wide and 25 mm. long were employed¹⁸. Resistance to tearing was evaluated by the American Society for Testing Materials test method, with specimens in the form of a crescent having one cut. For abrasion resistance, standard test-specimens were prepared for test on the du Pont-Grasselli machine by molding.

Time of resin condensation.—After numerous preliminary tests, a resin of the following mole composition was selected (preparation R₁) for a systematic examination:

Resorcinol	1
Formaldehyde (as 30% aqueous solution)	1
NaOH (as 1 N solution)	0.05
Fe (as 0.1 M FeCl ₃ solution)	0.0001

To a flask are added resorcinol, formaldehyde solution, and sodium hydroxide; the flask is stoppered and agitated rapidly, ferric chloride is added, and the condensation is allowed to proceed in the closed flask.

The reaction is exothermic and, to prevent precipitation, or too abrupt condensation, it is necessary to keep the temperature below 50° and above 25° C.

A series of resins was prepared in the above manner, using variable times of condensation. These resins, used in the proportion of 10 grams preparation R₁ to 100 grams of 60 per cent latex, gave the results indicated in Table II.

TABLE II
TIME OF RESIN CONDENSATION

Condensation time (min.)	Tensile at break (kg./sq. cm.)
20	300
40	350
60	450
120	450
180	445
240	455
300	450
360	450
Control, without resin	330

The reaction time is of great importance, and maximum reinforcement occurs only when condensation has been carried out for about 1 hour. For practical reasons (viscosity, hygroscopicity, etc.) it is preferable not to be beyond this time of condensation.

Influence of conditions of vulcanization.—The optimum vulcanization of control mixture M, without resin, corresponds to a heating of 1 hour at 100° C in hot air. It was necessary to determine whether the addition of the resin modified these conditions. By varying the time of vulcanization at 100° C or the temperature of heating for 1 hour, values for the tensile at break shown in Table III were found.

The addition of resin does not noticeably influence the conditions for optimum vulcanization, which are around 60 to 70 minutes at 100° C.

Proportion of catalyst.—The catalyst regulates the nature and the molecular weight of the components of the resin. It is not surprising to find, as shown in Table IV, that the concentration of the alkali in the reaction mixture directly influences the reinforcement.

It is sufficient to have a small quantity of iron, the optimum corresponding to the proportion given in preparation R₁. Less favorable results obtained in its absence show that iron enters into the catalysis; it can be replaced by other metals, such as tin or aluminum.

Molecular ratio of components.—The proportion of formaldehyde in preparation R₁ was varied between 0.5 and 3 moles, while remaining within the limits

TABLE III
EFFECT OF TIME AND TEMPERATURE OF VULCANIZATION

Influence of time of vulcanization at 100° C		Influence of temperature for 1-hour heating	
Min.	Kg./sq. cm.	T, ° C	Kg./sq. cm.
30	425	70	360
40	415	80	450
50	460	90	465
60	475	100	475
70	485	110	465
80	480	120	325
90	475	130	175
100	470	140	150
110	450	150	150
120	440		
130	440		
150	445		

TABLE IV
EFFECT OF CONCENTRATION OF CATALYST

Concn. of NaOH in preparation R ₁	Tensile at break (kg./sq. cm.)
0	200
0.01	330
0.02	400
0.03	425
0.04	435
0.05	360
0.06	475
0.08	480
0.10	455
0.12	390

of temperature indicated. The resin was incorporated with the latex 1 hour after the start of the condensation reaction.

Figure 1 shows the results of the measurements made on the vulcanizates. The molecular proportion of the components present is of primary importance.

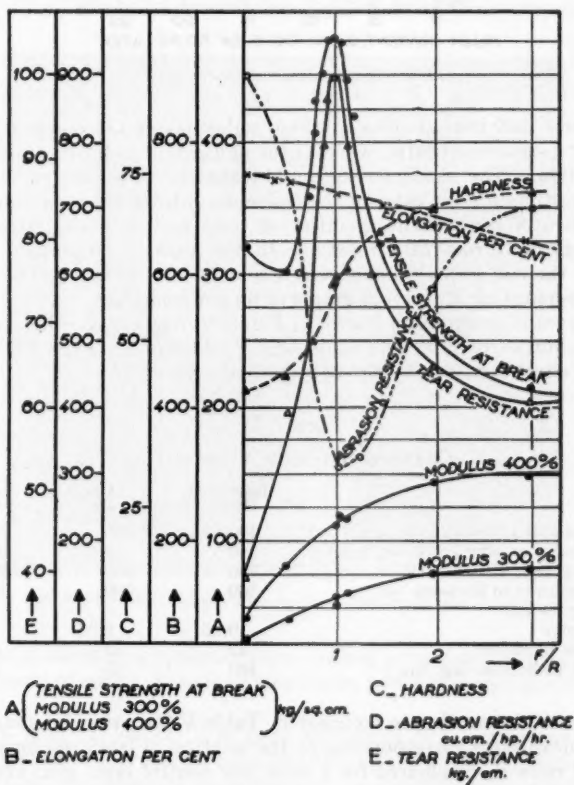


FIG. 1.—Influence of molecular ratio, F/R , on properties of mixes reinforced by 10 per cent of resin.

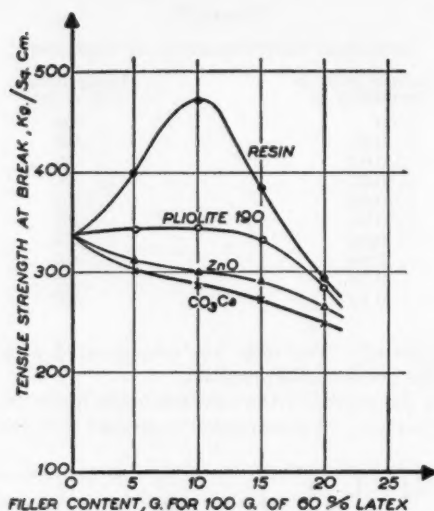


FIG. 2.—Tensile strength of reinforced latex.

The hardness and the modulus of these vulcanizates are increased with the formaldehyde-resorcinol ratio, whereas the elongation at break undergoes very little variation. The tensile strength and resistance to tearing and to abrasion display a maximum for a value of the molecular ratio in the neighborhood of 1.

Proportion of resin.—The quantity of resin added to the latex plays an equally important role with reference to the various properties. Figure 2 shows that there is a maximum of reinforcement for a proportion of around 10 grams of preparation R₁ for 100 grams of 60 per cent latex.

The curves of comparison shown in Figure 2, relating to other loading materials (calcium carbonate, zinc oxide, and Pliolite, Latex Type 190) make the reinforcing effect obtained by the new method evident.

TABLE V
CHARACTERISTICS OF VULCANIZATES

	Reinforced latex	Latex control	Carbon black mix
Tensile at break (kg./sq. cm.)	460	330	310
Modulus at 300% (kg./sq. cm.)	60	15	100
Elongation at break (%)	750	750	500
Resistance to abrasion (cc./hp./hour)	300	600	350
Density	0.95	0.93	1.2
Shore hardness	62	42	68
Tear resistance (kg./cm.)	100	50	90

It appeared interesting to compare in Table V the principal characteristics of three vulcanizates corresponding to the mixture of latex reinforced with 10 per cent of resin R₁ condensed for 1 hour; the control latex mix; and a carbon black mix, prepared by mastication (typical tire tread stock), vulcanized in a press for 60 minutes at 143° C:

Smoked sheet	100
Zinc oxide	6
Stearic acid	3
Sulfur	2.85
Pine tar	2
Phenyl-2-naphthylamine	1
Mercaptobenzothiazole	0.75
MPC black	40

It is seen that the vulcanizate of reinforced latex has remarkable properties, clearly superior to any present known properties of rubber.

Other characteristics not set forth in Table V are likewise very good, for instance, permanent set and resistance to flex cracking are comparable to those of the control latex. In comparison to a carbon black tread stock, the dielectric properties are better and the thermal conductivity is greater, while the heat build-up on the Goodrich flexometer and traction hysteresis are slightly lower. Aging is excellent.

Figures 3 and 4 show the characteristic appearance, after breaking, of the test-pieces used for traction and tear resistance. Instead of the clean-cut sections which are usually observed, the material here shows a ragged rupture.



FIG. 3.—Tensile test-pieces after rupture. Reinforced latex on right.

Influence of vulcanizing system.—Ingredients of normal mix.—This compound contains 2 parts of sulfur, 3 parts of zinc oxide, and 1 part of zinc diethyldithiocarbamate.

It can be seen (Table VI) that small variations individually in the proportions of each of these ingredients have no effect on the tensile strength and that, for each of these, the optimum corresponds to the quantity utilized in the normal mixture.



FIG. 4.—Tear test-pieces after testing. Reinforced latex on right.

On the other hand, if the three ingredients are varied simultaneously by adding different proportions of the normal dispersion to the latex, *e.g.*, 5 to 20 per cent by weight, significant changes are observed. The hardness and the modulus increase very nearly linearly with the percentage of ingredients, and the elongation at break diminishes, while the resistance to tear, to rupture, and to abrasion passes through a very sharp maximum for a portion of 10 parts by weight. The tensile strength values are, respectively, 325, 460, 370, and 270 kg. per sq. cm. for 5, 10, 15, and 20 parts loading of ingredients.

Other accelerators.—If the effect of different types of accelerators is examined, it is observed that many of them do not function in the presence of the resorcinol-formaldehyde resins. Vulcanization is very much retarded or does not take place at all. It is possible that the chemical constitution of the accelerator permits reaction with the partially condensed resin.

The dialkyldithiocarbamates give the best results; in particular, cadmium diethyldithiocarbamate makes possible vulcanization at 120° C in hot air, with an extended plateau.

Influence of drying conditions.—The drying conditions employed in these experiments were determined empirically.

TABLE VI
INFLUENCE OF VULCANIZING SYSTEM

Influence of sulfur		Influence of zinc oxide		Influence of zinc diethyldithiocarbamate	
% S	Kg./sq. cm.	% ZnO	Kg./sq. cm.	% Accel.	Kg./sq. cm.
0.5	275	1	420	0.5	170
1	440	2	475	0.75	275
1.5	450	3	475	1	470
2	475	4	460	1.25	465
2.5	470	5	455	1.5	450
3.5	460	7.5	460	2	415
5	445	10	455	3	385

By eliminating the period of drying in ambient air, which is difficult to control, by use of a ventilated oven (air circulation of 1600 liters per hour with a capacity of 0.2 cu. meter) and by adjusting air to normal humidity, the authors have been led to some interesting observations.

First of all, during the period in the oven, vulcanization may be made to take place at the same time as the drying; furthermore, the mechanical properties are further improved, and thus vulcanizates can be obtained with tensile strength of 530 kg. per sq. cm., and tear resistance values of the order of 130, and, under certain conditions, of 160 kg. per cm.

It is equally possible, with good results, to combine a drying time of shorter duration, for example at 30° or 40° C, with a complementary vulcanization of 1 hour at 100° C in hot air (Table VII).

TABLE VII
EFFECT OF DRYING CONDITIONS

Conditions of drying and vulcanisation		Tensile at break (kg./sq. cm.)
Days	° C	
4	40	520
2.5	50	530
1.5	60	495
2	30	500
1 hour	100	
2	40	480
1 hour	100	

By contrast, if drying is effected under the conditions generally recommended for objects molded from latex—with an initial high humidity decreasing progressively with an increase in temperature—reinforcement does not take place.

The drying conditions are thus of primary importance.

Aging of vulcanizates.—The good aging of the vulcanizates is another condition indispensable to their technical value. Therefore, the behavior in the Geer oven, at 70° C, of a vulcanizate of latex reinforced with 10 per cent resin has been compared with a control mixture of latex without resin. The results are indicated in Table VIII.

TABLE VIII
EFFECT OF AGING

Days at 70° C	0	2	5	10	20	30	40
Reinforced latex							
Tensile at break (kg./sq. cm.)	470	460	450	420	400	370	340
Loss (%)	—	2	4	11	15	21	28
Control latex							
Tensile at break (kg./sq. cm.)	320	335	325	295	235	190	170
Loss (%)	—	—	—	8	26	40	47

The vulcanizate made with reinforced latex, without additional antioxidant, has normal aging, rather better than that of the control latex, which is known to exhibit good aging. In addition, after 40 days in the Geer oven, the mechanical properties are still superior to those of an unaged latex mix without resin.

CONCLUSIONS

These experiments show that it is possible, by addition of certain partially condensed resins to latex under suitable conditions, to realize a pronounced reinforcement, the vulcanizates presenting a combination of exceptional mechanical properties. The way is thus open for the direct use of latex in applications (which could not be thought of until the present) requiring resistance to tear, high modulus, and hardness.

There still remain points to clear up and improvements to make before such a method can be employed technically. Improvements are needed in controlling stability and extending the range of vulcanization conditions. The studies which have been pursued in this direction have given encouraging results; moreover, either with or without the addition of ordinary loading materials, the procedure lends itself to many practical applications.

From a theoretical point of view, the authors offer no hypothesis on the mechanism of this reinforcement; the observations involved are recent and the example of the extensive studies carried out on the mechanism of the reinforcement of milled rubber with carbon black suggests caution. It does not appear, however, that the resins intervene directly in the vulcanization; the operating conditions and the proportions are very different from those indicated in the work of van der Meer and the Rubber-Stichting¹⁹. Nor does there seem to be a simple chemical combination of the resins to the rubber, inasmuch as the curve of Gee²⁰, relating the swelling in various solvents to their energy of cohesion, does not show displacement of the maximum in comparison to the latex control.

Many years may elapse before it will be possible to provide a satisfactory explanation of this phenomenon, thanks to which vulcanizates of natural rubber have been given a combination of properties never before attained.

SUMMARY

The direct utilization of latex has up to the present time been limited to a relatively small number of applications because of lack of knowledge of how to communicate to articles sufficient hardness, modulus, resistance to tearing, and resistance to abrasion. It is possible to obtain such properties by combining the molding of latex (thermosensitized by the action of trypsin) with the addition of partially condensed resins.

Numerous types of resins can be utilized, but the best results have been obtained by resorcinol-formaldehyde resins. The mechanical properties of vulcanizates thus prepared are extremely high—for example, the tensile strength may reach 7500 pounds per square inch (with an elongation of 700 per cent), and the resistance to tearing 900 pounds per inch.

Operating conditions that must be observed for the formation of the resin are described in detail, as well as the influence on the properties of vulcanizates of different factors: length of condensation of the resin, conditions of vulcanization, proportion of catalyst, molecular ratio of constituents, conditions of drying, etc. A new way is opened for obtaining vulcanizates of natural rubber of outstanding mechanical properties.

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THE CHEMICAL CONSTITUTION OF CHLORINATED RUBBER *

RENÉ ALLIROT

INTRODUCTION

Under the designation of chlorinated rubber are grouped a whole series of products obtained by different processes, all of which furnish plastic substances containing 60 to 66 per cent of chlorine. The contributions of various investigators which will be cited deal only with products which are formed by the prolonged action of chlorine gas on natural rubber in solution in carbon tetrachloride.

This reaction has been the subject of a number of studies, as a result of which various empirical formulas for chlorinated rubber have been assigned.

McGavack¹ and also Baxter² concluded that the composition is $(C_{10}H_{12}Cl)_n$. Kirchhof³ and Nielsen⁴ give $(C_{10}H_{12}Cl)_n$, and Bloomfield⁵ $(C_{10}H_{11}Cl)_n$. These differences in empirical formulas can, perhaps, be best explained by an observation of Staudinger and Staudinger⁶, according to which the chlorine content should vary with the molecular weight of the polyisoprenes to the chains of which chlorine has been fixed, either by addition or by substitution.

To throw light on the distribution of chlorine among the individual components of chlorinated rubber, a series of samples of chlorinated rubber was prepared, the products were fractionated by precipitation, and the chlorine content of each fraction was determined.

METHOD OF PREPARATION

Natural rubber was dissolved in carbon tetrachloride so that the concentration of rubber was 3 per cent by weight. The solution was heated to 50° C and was treated with a current of chlorine gas until no more chlorine was absorbed. After elimination of excess chlorine, the solution was poured into water at 90° C, which expelled the solvent and precipitated the chlorinated rubber in the form of white flocks. The product was then dried in an air oven at 90° C.

METHOD OF FRACTIONATION

The product was dissolved in toluene, the insoluble impurities were filtered off, and several fractions were then successively precipitated in the form of coacervates by repeated additions of ethanol. These coacervates were dissolved in toluene, and the solutions were poured into ten times their volume of boiling methanol⁷. In this way the chlorinated rubber was precipitated in the form of flocks, and simple heating of the product in an air oven for several hours at 70° C was sufficient to free it of all traces of solvent. The first fraction precipitated was always slightly colored because of the presence of impurities, and these made the analytical results uncertain.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, Vol. 231, No. 20, pages 1065-1066, November 13, 1950.

DETERMINATION OF CHLORINE

The chlorine in each fraction was converted to an inorganic form by the sodium peroxide method⁶; then it was determined potentiometrically in sulfuric acid medium by silver nitrate. By proper standardization of the reagent and of the solutions, it was possible to determine the chlorine with an absolute precision of 0.5 per cent, as was proved by control tests.

The chlorine contents of the different fractions obtained from the different preparations are shown on the following table.

Sample no. 1		Sample no. 2	
Fraction	Percentage chlorine	Fraction	Percentage chlorine
1	58.0	1	63.6
2	65.2	2	65.5
3	65.4	3	65.4
4	65.4	4	65.5
5	65.2	5	65.7
6	65.8	6	65.4

The first fraction of each sample had a chlorine content definitely lower than the chlorine contents of the other fractions. This may be attributed primarily to the presence of impurities, because the relatively high degree of purification to which Sample no. 2 was carried before fractionation made this difference much smaller. On the contrary, all other fractions had the same chlorine content, that is, 65.5 per cent, or within the range of experimental errors. The theoretical chlorine contents corresponding to the various empirical formulas which have been proposed are 68.24 per cent for $(C_{10}H_{12}Cl_3)_n$, 65.42 per cent for $(C_{10}H_{11}Cl_7)_n$, and 65.08 per cent for $(C_{10}H_{13}Cl_7)_n$.

CONCLUSIONS

The results of the work described in the present paper indicate that, by the prolonged action of chlorine on polyisoprenes, chlorinated compounds corresponding to the composition $(C_{10}H_xCl_7)_n$ are formed, irrespective of the molecular weight. The exact hydrogen content of these products can be calculated from determinations of the hydrogen chloride evolved in the reaction, and measurements to this end are in progress. Furthermore, determinations of the osmotic pressure and intrinsic viscosity, which have already been undertaken, should make it possible to determine with certainty the mean degree of polymerization of each fraction.

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STUDY OF BONDED UNITS *

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The evaluation of the strength of a bonded unit involves a study of the component parts, and for convenience these can be regarded as the bond, the rubber, and the metal. In the present paper the discussion is confined to the fundamental development of testing techniques.

It is essential at the outset to appreciate clearly and exactly what property is being measured, and two of the present authors¹ have recently discussed and differentiated between methods of testing bonding agents and bonded units. There is an important distinction between the two cases; although it is apparently easy to impose a stress on a bonded unit, it is not always a simple matter to assess the results of stressing. On the other hand, it is difficult to ensure that the strength of the bond is being measured, as, even when bonding agents are tested under optimum conditions, the test-pieces are in effect bonded units and failure occurs at the weakest point, which may not be at the bond.

It is not proposed to review the many methods of testing special bonds between rubber and metal articles, but it seems desirable to call attention to the many methods proposed by Werkenthin². The normal A.S.T.M. test³ is, however, probably the most widely used general test in the rubber-metal bonding field. Previously¹ objections to the method were summarized in the following points:

1. The test bore no relation to service conditions, and in service early failures are often due to shock and fatigue and seldom due to slow loading, but it is not suggested that the proposed method simulates all service conditions.

2. The method using a layer of rubber 0.5 inch thick is often used as a test for bonding agents, whereas it is the strength of the unit that is being measured.

3. There is a nonuniform distribution of stresses throughout the test-piece, and the more the test-piece deforms, the more it necks, and a shear component of stress develops near the junction of the rubber and the metal. This difficulty is met when different thicknesses are used or when compounds of different hardnesses deform to different extents.

4. With some types of material it is extremely difficult to obtain reproducible results using the method.

5. The method does not discriminate clearly between different types of bonding agent.

It is understood that the degree of objection to (2) and (3) depends on the softness of the rubber stock.

In view of the above objections to the normal method, the authors decided to use an impact test and designed a falling-weight method¹.

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 373-381, February 1951. This paper was presented at the International Meeting of the Division of Rubber Chemistry of the American Chemical Society, Cleveland, Ohio, October 11-13, 1950.

The test-piece is attached to the bottom of the central column and a circular metal disk is screwed into the underside of the test-piece (Figure 1). An adjustable collar can be moved to any position on the central column and clamped at any desired height. The weight is pulled up by a rope which passes down the inside of the hollow central column. The rope is attached to the three parts of the weight support, and, as the weight is raised to the level of the clamped

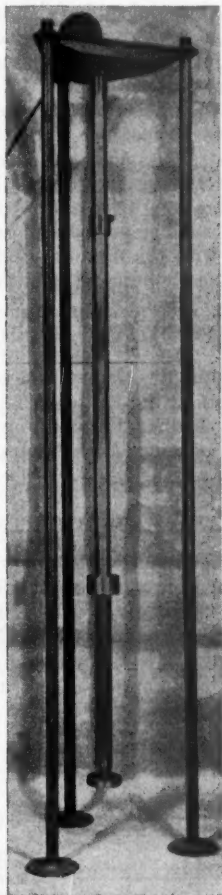


FIG. 1.—Falling weight impact tester.

cylinder, the projections of the weight support are pushed into the center of the hollow column. As the top of the weight reaches the bottom of the clamped cylinder, the projections are pressed back sufficiently to release the weight and it falls down the tube onto the test piece.

With this apparatus the energy input can be varied from 1 to 300 foot-pounds and the velocity at impact from 8 to 20 feet per second.

The results obtained with the falling-weight method may be examined from the point of view of the five objections listed above against the conventional straight pull test.

The first is axiomatic, and in the authors' opinion the falling-weight test approaches service conditions more closely, especially when the results are interpreted in conjunction with fatigue tests¹. Earlier results showed conclusively that when bonding agents are tested, whether the impact or the straight pull test be employed, the thickness of rubber should be kept to a minimum, and a maximum thickness of $\frac{1}{16}$ inch was recommended.

Nonuniform distribution of stresses throughout the test-piece is present, whether the impact or straight pull method is used. The previous paper stated that the deformation of the test-piece had been reduced by testing under the high impact velocities of 8 to 20 feet per second. This belief was based on some rather crude check tests, but more recently high-speed photographs of the deformation under impact have shown that for a fixed stress—*e.g.*, 400 pounds per sq. cm.—the elongation of the test-piece is approximately the same whether the rate of straining is 1 inch per minute or 12 feet per second. At the rates of straining attainable with the present apparatus, there is no reduction in the elongation of the test-piece compared with the straight pull test at 1 inch per minute.

The question of the reproducibility of results obtained with the impact method is discussed below.

The impact method discriminates clearly between different bonding agents, whereas the straight pull method did not discriminate between them and, in fact, its results would have classified the bonding agents as equally efficient. The improved discrimination obtained with the impact test is one of the main factors justifying its use.

APPARATUS AND EXPERIMENTAL METHOD

Figure 2 shows a schematic layout of the apparatus.

The principle of the method of measuring the forces occurring in a bonded unit under impact extension was to use four electrical resistance strain gage units connected in a Wheatstone bridge network (Figure 3).

Two of the gages, T_1 and T_2 , were mounted on a dynamometer bobbin carrying the bonded unit. On extension of the rubber unit under impact, T_1

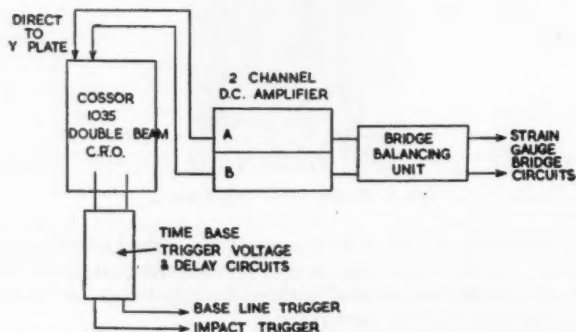


FIG. 2.—Block diagram of experimental layout.

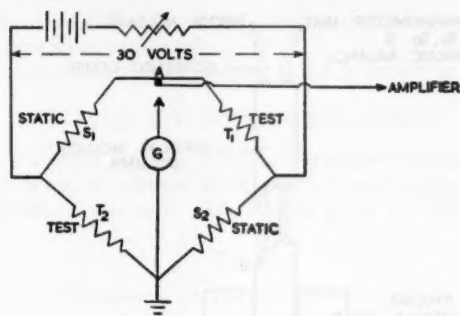


FIG. 3.—Strain-gage bridge.

- A. Bridge balancing resistance, sliding contact on 8 inches of Nichrome wire
 G. Galvanometer, 5-cm. deflection per microampere
 S_1, S_2 . 1000 Ω strain gages mounted on similar dynamometer unit but not subject to impact
 T_1, T_2 . 1000 Ω strain gages mounted on same dynamometer unit carrying bonded sample under test
 Output voltage from bridge on impactive straining of T_1 and T_2 , in range 0 to 8 mv. corresponding to load on bonded unit of 0 to 2500 pounds

and T_2 are strained by the dynamometer bobbin, and the resulting out-of-balance voltage of the bridge is amplified and fed to the Y plate of a Cossor 1035 double beam cathode ray oscillograph.

The voltage applied to the bridge network was controlled at 30 volts throughout, and final bridge balancing for zero e.m.f. output was accomplished by a sliding contact on Nichrome wire. A bridge voltage check and bridge balance check were carried out before every impact series.

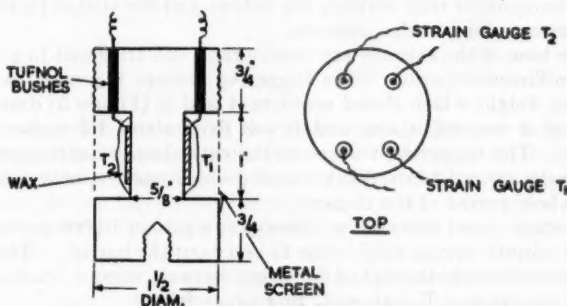


FIG. 4.—Dynamometer unit.

Figure 4 gives details of the assembled dynamometer bobbin, made from high-tensile steel. The strain gages were affixed to the spindle by the standard technique and covered with wax. To avoid breakage of the connections to the strain gages, leads of thick tinned copper wire were fixed rigidly in Tufnol bushes, set in one flange of the bobbin. A similar unit carrying the two strain gages S_1 and S_2 completed the network of Figure 3. A thin cylindrical metal cover excluded drafts from the strain gages, the bridge network remaining stable over long periods.

Figure 5 shows the falling weight impact apparatus in schematic form, set up with a dynamometer bobbin for measuring stress on the upper surface of

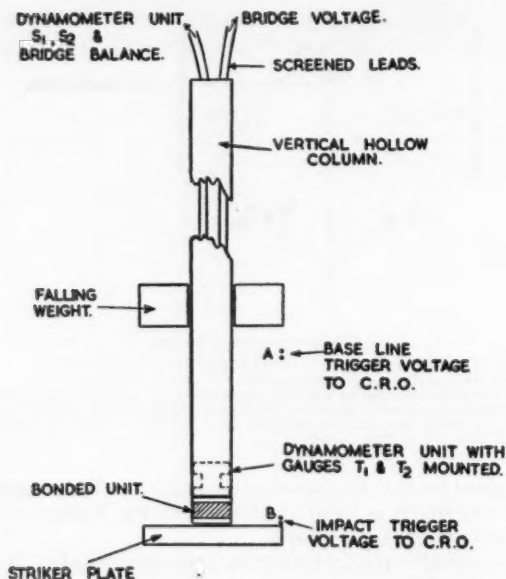


Fig. 5.—Impact tester for measuring stress.

the bonded unit. Stress on the lower surface was also measured by introducing a similar dynamometer unit between the rubber and the striker plate and completing a corresponding bridge network.

The time base of the cathode ray oscillograph was triggered to give a single scan of 50-millisecond period. The triggering voltage (18 volts) was applied by the falling weight which closed contacts *A* and *B* (Figure 5) during its fall. The height of *A* was adjustable and *B* was fixed about 1.5 inches above the striker plate. The triggering voltage to the cathode ray oscillograph was applied via condenser-resistance delay circuits which ensured only a single scan within the whole period of the impact.

The two-stage direct current amplifiers gave a gain of 10,000 and were stable over about 1 minute, giving ample time to carry out the impact. The transient force-time trace was photographed for every impact, using a standard Cossor oscillograph camera and Kodak recording paper RP.30.

The dynamometer unit could be mounted in the Denison heavy-duty tensile machine and the bridge network calibrated directly against a potentiometer, giving a calibration curve of force (pounds) against out-of-balance voltage

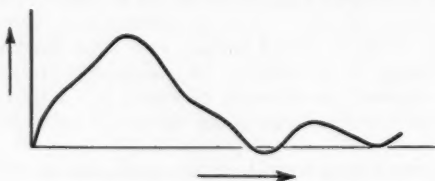


Fig. 6.—Stress-time curve.

(mμ). This was linear of slope, 312 pounds per millivolt. Before use, each day, the amplifiers were calibrated.

A typical stress-time curve as photographed is shown in Figure 6.

TOP AND BOTTOM STRESSES

It was first necessary to check whether the stress developed at both bonded surfaces was the same, or whether the stress at the top surface was lower, owing to the deformation of the unit. The results given in Table I illustrate that

TABLE I
COMPARISON OF TOP AND BOTTOM FORCES

Test piece	Energy input (foot-lb.)	(a) Bottom force (lb.)	(b) Top force (lb.)	(a)-(b) (lb.)
Standard tread, 0.5-inch thick rubber	40	1000	1110	-110
		1130	1110	+20
		1040	1050	-10
		1150	1130	+20
		1160	1130	+30
		1130	1080	+50
		1010	990	+20
		1070	1080	-10
		1010	1030	-20
		1040	1030	+10
Standard tread, $\frac{1}{8}$ -inch thick rubber	17.5	1400	1450	-50
		1400	1420	-20
		1300	1320	-20
		1360	1350	+10
		1330	1320	-20
		1300	1230	-20
		1330	1350	-40
		1330	1370	-40

within the experimental error of the measurements there is no significant difference between the top and bottom stresses. It therefore seemed reasonable to measure only one of these stresses and for various reasons it was more convenient to measure the top stress; throughout the remainder of the present paper the stresses quoted have been measured by means of strain gages placed above the test-piece.

In Table II results are given for the forces developed with successive blows on three different test-pieces cured at the same time from a single batch of natural rubber tread but tested on different days. This gives an indication of the reproducibility of the method.

Several interesting points arise from the results in Table II, but the immediate point of interest is that the highest forces developed in the three test-pieces are 2150, 2100, and 2160 pounds, and a range of 60 pounds on 2100 pounds can be regarded as satisfactory.

The fact that the force increased with successive blows is discussed more fully in the next section.

EFFECT OF CONDITIONING

Table II shows that with successive blows the force developed in the tread stock increases and passes through a maximum. At first sight this behavior is

TABLE II
FORCE DEVELOPED WITH SUCCESSIVE BLOWS

Test-piece, rubber 0.25 inch thick	Energy input (foot-lb.)	Date	No. of blows	Force (lb.)
A	60	5/24/50	1	1810
			2	1950
			3	2150
			4	—
			5	2080
B	60	5/25/50	1	1770
			2	1940
			3	2000
			4	2100
			5	2030
C	60	5/31/50	1	1710
			2	1870
			3	2010
			4	2100
			5	2160

anomalous, because prestressing produces softening up to the point of pre-stressing. This effect was therefore studied in closer detail.

Gum and tread stocks were used to show that the increase in force was connected with changes in the rubber-carbon and carbon-carbon structure. In both cases the effect was investigated from various energy levels; the results for the gum stock are given in Table III and the tread stock in Table IV.

GUM STOCK		TREAD STOCK	
Pale crepe	100	Smoked sheet	100
Zinc oxide	5	Zinc oxide	5
Stearic acid	1	Kosmobile-HM	47.5
Sulfur	2.5	Stearic acid	3
Mercaptobenzothiazole	0.5	Sulfur	3
Cure 30 minutes, 141° C		Mercaptobenzothiazole	0.85
		Cure 50 minutes, 141° C	

From Table III it is clear that with the gum stock the force developed is constant within experimental error until it decreases just before break occurs.

The results in Table IV are presented in graphical form in Figure 7 for clarity. The following points emerge:

With input energies of 40 foot-pounds and above, the force increases with successive blows, passes through a maximum value, and decreases before rupture occurs.

With input energies of 20 foot-pounds the force either remains constant or decreases with successive blows.

With input energies of 10 foot-pounds the force decreases with successive blows.

In the second experiment, using an input energy of 60 foot-pounds, the test-piece was rested for 30 minutes between the fifth and sixth impacts. There is slight evidence of some recovery, but it is of doubtful significance, and much longer times would have to be used before appreciable recovery occurred.

TABLE III
EFFECT OF CONDITIONING ON FORCES DEVELOPED IN GUM STOCK
(Test piece, gum stock 0.5-inch thick rubber)

Input energy 120 foot-lb.		Input energy 90 foot-lb.		Input energy 60 foot-lb.		Input energy 40 foot-lb.	
No. of blows	Force (lb.)	No. of blows	Force (lb.)	No. of blows	Force (lb.)	No. of blows	Force (lb.)
1	1770	1	1000	1	720	1	550
2	1770	2	1100	2	750	2	550
	Break	3	1030	3	780	3	560
		4	1060	4	780	4	580
		5	1060	5	750	5	560
		7	1090	7	800	7	580
		10	990	10	800	8	530
		15	—	15	720	9	570
		16	940	19	Break	10	530
			Break			11	550
						13	470
						16	500
						17	540
						21	510
						24	510
							Not broken

TABLE IV
EFFECT OF CONDITIONING ON FORCES DEVELOPED IN TREAD STOCKS

No. of blows	Energy input (foot-pounds)					
	60	60	40	20	20	10
	Weight (pounds)					
	20	20	10	10	5	5
	Height (feet)					
	3	3	4	2	4	2
Interval between blows (seconds)						
	30	30	30	30	30	30
Force (pounds)						
1	1801	1770	1470	1430	1310	1290
2	1950	1940	1590	1380	1290	1180
3	2160	2000	1640	1450	1260	1170
4	—	2100	1640	1450	1220	1200
5	2080	2030	1670	1380	1230	1140
6	2150	Rested 0.5 hour	Not broken	Not broken	Not broken	Not broken
7	2080	1970				
8	2170	2050				
9	2120	2000				
10	1970	1990				
11	1770	1950				
12	1660	Not broken				
13	1530					
14	940					
	Break					

The interval of 30 seconds between successive impacts is the shortest practical time that could be used if the force-time curves were to be photographed, as various timing switches had to be reset between impacts.*

The first three points are easily explained if the effect of prestressing on the normal stress-strain curve is considered from the point of view of constant energy input. In Figure 8 the effect of prestressing on the "static" stress strain curve of the natural rubber tread is shown. It illustrates that, for a fixed low energy input, the stress is lower with the subsequent stretches than for the initial stretch. For a fixed high energy input, the stress is higher with

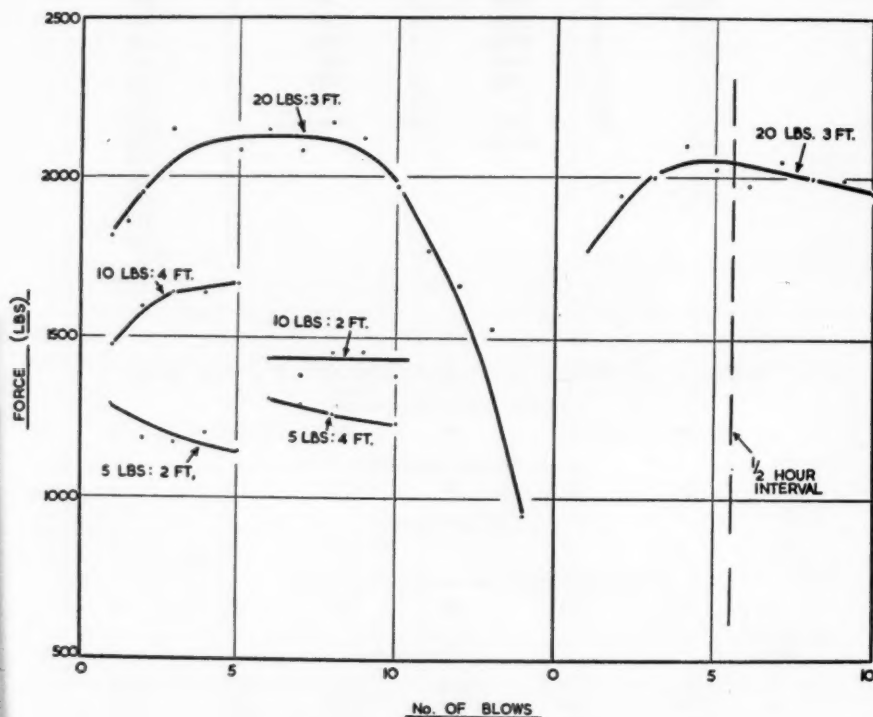


FIG. 7.—Change of force with successive blows.

subsequent stretches than on the initial stretch. From this crossover it is clear that there is an intermediate energy input, where it is possible for the stress to remain practically constant with the subsequent stretches, and this has been checked experimentally. In the case of the higher energy inputs, the steeper gradient of the stress-strain curve at the higher elongations on the subsequent deformations suggests that a greater degree of crystallization and (or) alignment can be produced by the same energy input after the initial filler structure has been broken down. When this occurs, the rubber is effectively harder in the sense that a higher stress (on subsequent deformations) is pro-

duced by the fixed energy input. Interpretation of the effect of prestressing on "static" stress-strain curves from energy considerations therefore gives results in accord with those obtained from the impact test and the apparent anomalies are resolved.

Previous explanations of the prestressing phenomena⁴, where it has been stated that the rubber on subsequent stretches is softer up to the point of prestressing, have not dealt with energy considerations. These explanations are not sufficient and can give rise to misleading conclusions.

At the present time when prestressing is being considered by Committee TC45 (Rubber) of the International Organization for Standardization, it is important to realize that prestressing under constant load, constant strain, or constant energy does not necessarily give the same results, and the choice of the

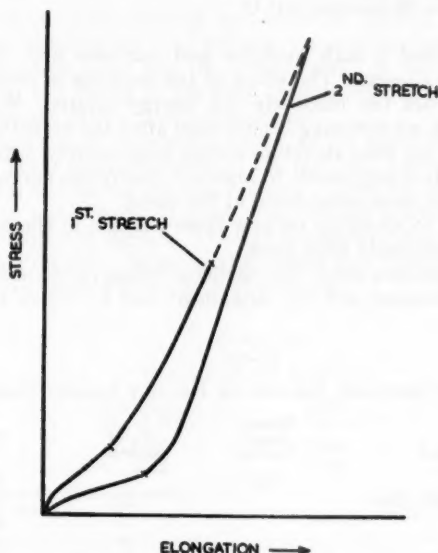


FIG. 8.—Static stress-strain curve.

conditions for prestressing depends on the particular service conditions governing the problem being studied. For example, different parts of a tire can operate under different conditions⁵, and prestressing to a constant energy input should be carried out only on compounds to be used in parts of a tire where conditions of constant energy predominate throughout the life of that particular portion of the tire.

Certain compounds containing high volume loadings of "structural" fillers, *e.g.*, magnesium carbonate, silene, Frantex, etc., are extremely hard. If these compounds are exercised by flexing, progressive softening can occur along the line of flexing, but the stiffness of the compound is maintained throughout the first few flexings and then the progressive softening begins suddenly. A compound containing Frantex-B (Compound T.6021) was made and evaluated by

the impact method and also by static hysteresis loops. The results obtained by the impact method are given in Table V.

COMPOUND T.6021	
Pale crepe	60
Isolac	40
Stearic acid	1.5
Titanium dioxide	10
Frantex-B	36
Sulfur	3
Vulcafor-F	1.25
Zinc oxide	5
Paraffin wax	2
Turkey red oxide 2GS	3
Vulcafor fast brown BS	1.5
Kosmos No. 1	0.5
Cure 30 minutes, 141° C	

The test-piece had a high modulus and hardness and, therefore, small energy inputs were chosen. The effect of the modulus is seen from the high forces developed from the relatively low energy inputs. With a 5.2 foot-pound energy input, no softening occurs until after the seventh blow. Thereafter breakdown of the filler structure occurs progressively until breakdown of the bond occurs. It is impossible to separate clearly the effects of breakdown of the filler structure from breakdown at the bond.

It is interesting to speculate on how these changes in the modulus on subsequent deformations could take place.

In the case of the gum stock, the particles (whatever they may be) are free to undergo crystallization and (or) alignment and to return to their original state of disorder.

TABLE V
EFFECT OF REPEATED IMPACTS ON HEAVILY LOADED COMPOUND

Test-piece	Energy input (foot-lb.)	No. of impacts	Force (lb.)
T.6021, 0.25 inch thick	5.2	1	2040
		2	2080
		3	2040
		4	1970
		5	2000
		6	1930
		7	1950
		8	1770
		9	1600
		11	1420
		13	1280
		14	530
			Break

In the case of reinforced stocks, small inputs break up the initial fortuitous structure and the degree of alignment of the particles is small. The stock is thereby softened.

In the case of reinforced stocks, large energy inputs break up the initial filler structure, but there is sufficient energy available to produce considerable alignment of the rubber and of the filler particles in the later stage of the deformation. It is probable that the friction introduced by the reinforcing filler

impedes the equivalent return of the rubber to the original state of disorder. Subsequent constant but large energy inputs therefore produce more easily a higher state of alignment than that produced by the earlier blows, with the result that the rubber appears to be harder. There would be no noticeable effect if later blows were limited to small energy inputs which could not take advantage of the greater ease of alignment.

In the case of the heavily filled stocks (especially with such fillers as magnesium carbonate) there is a minimum energy input, which may be fairly high, to break up the fortuitous structure of the filler. After this structure has been broken the stock behaves, on subsequent stressing, like any other filled stock in which the fortuitous structure has been destroyed.

TESTING THE BONDED UNIT

The evaluation of the bonded unit involves: testing the efficiency of the bonding agent, including the bond between the bonding agent and the metal and between the bonding agent and the interply stock or the rubber stock; testing the efficiency of the design of the unit; testing the quality of the rubber; and testing the strength of the metal components.

It is not proposed to discuss the fourth, as the metal components are normally regarded as the strongest parts of the unit and suitable standard methods of testing metal test-pieces are well known. However, it is possible to design units where the metal parts (if made from certain alloys) may not withstand the stresses imposed in service, whereas the rubber and bonding agents may have sufficient strength. In such cases, where new metal parts are being used, it is advisable to check the strength of the metal.

TABLE VI
EFFICIENCY OF CEMENTS

	Straight pull (lb./sq. inch)	Shear (lb./sq. inch)	Impact strength (foot-lb.)
CDR* cement	1430	1645	76
PI* cement	1515	1745	160

* CDR = Chlorine derivatives of rubber
PI = Polyisocyanate

Bonding agent.—Before a bonding agent is chosen for a given application it is necessary to evaluate its characteristics thoroughly. Two of the present authors have compared¹ the relative efficiencies of chlorine derivatives of rubber cements and polyisocyanate cements in straight pull, shear, and under impact and obtained the results reported in Table VI.

These results were obtained with test-pieces having a $\frac{1}{16}$ -inch thick layer of natural rubber tread, which is the thickness of rubber recommended for evaluating bonding agents. This is done in an attempt to ensure that the minimum amount of energy is absorbed in the process of deforming the rubber. It would be better to have even a thinner layer of rubber than $\frac{1}{16}$ inch, but this is hardly practicable. The results given in Table VI show clearly the improved discrimination obtained with the impact method over the two more conventional testing conditions.

All the above methods are of interest only when evaluating new bonding agents or providing background information on established products. Technologists concerned with production of large numbers of bonded units are also

faced with the problem of testing their current production. One method of giving a routine check on the bonding agent would be to prepare nine A.S.T.M. disks with a $\frac{1}{16}$ -inch layer of the rubber compound used, and subject the test-pieces to ten successive blows from a known energy input, *e.g.*, 60 foot-pounds. If 50 per cent or more of the test-pieces withstand this treatment, the bonding agent can be regarded as behaving normally. The number of test-pieces and the energy input should be decided after a close study of each particular problem, and the figures given above are tentative illustrations and should not be regarded as definite recommendations for all types for of bonding agents.

In all bonding applications, the maximum stresses the bond is likely to meet throughout its life should be known approximately. If this desirable state of affairs exists, then, using the falling-weight method, it is possible to choose an energy level which produces the required stress on the bond and the stress can be measured by means of the strain gauge-cathode ray oscillograph technique. Having fixed the energy input in this way, it is necessary only to check the stresses developed on one of the test-pieces from each batch of manufacture. Where the service stresses are not known, initial experiments should be carried out with input energies producing a stress of 1000 pounds per square inch.

Efficiency of design of unit.—The design of a good bonded unit involves among other things protection of the bond against high stresses by utilizing the deformation characteristics of the rubber. The absorption of energy by the rubber reduces the maximum shock on the bond, and hence the unit will be protected by using as soft and as thick a rubber as the limits of strength, stability, and space permit¹. The correctness of this view is illustrated by the results where the peak force developed in units having different thicknesses of rubber has been measured.

In the previous paper¹ it was shown that, as the thickness of the test-piece was decreased from 1 inch to $\frac{1}{16}$ inch, the peak force increased from 630 to 2110 pounds for a constant energy input of 55 foot-pounds. Thus increasing the thickness of rubber from $\frac{1}{16}$ to 1 inch reduced the maximum stress imposed on the bond by as much as 70 per cent. Some of the implications merit further discussion. The results clearly indicate the advantages of using bonded rubber springs, and the important factors are to have a sufficiently large volume of rubber with a modulus such that a large proportion of the input energy is consumed in deforming the unit. On the basis of these results, two measurements are of prime interest to design engineers and rubber technologists: the maximum stress the bond will withstand (this measurement can be made using disks with a $\frac{1}{16}$ -inch layer of rubber); and the stress developed in test-pieces containing either the same volume of rubber as the service unit or a known proportion of the service volume. From these two measurements the bonding technique is checked, and the difference between the two stresses can be used as a measure of the efficiency of the design. As more accurate data on the stresses involved in service become available, it should also be possible to make more exact use of this type of information.

One possible application of the method would be in the development of suitable compounds for use in buffer stocks. After checking to be sure that the bond with the new compound is sufficient, the volume required to give the same decrease in stress as the original compound should be chosen, and the exact original volume should not be blindly replaced. The effects of fatigue and other important properties should still be measured, and the above procedure is suggested as an addition and not a replacement to existing practice.

Another implication of the above results is that if units having different

volumes of rubber are to be compared under comparable conditions of stressing, the input energy must be increased for the greater volumes so that the same stress is produced in each case.

Previously it was calculated¹ that:

$$I = \frac{S^2 A}{2E} \times l$$

where I = energy of impact, S = stress, E = Young's modulus, A = area of test-piece, l = length of test-piece.

The above equation means that the energy of impact and the stress are governed by the volume and modulus of the unit.

A rough check on the above formula has been provided from the measurements of hysteresis loops under impact on a range of thicknesses of cylindrical samples of natural rubber tread, of 2-square inch section.

The deformation of these test-pieces was photographed, using a high-speed camera operating at 3000 frames per second, and the camera and the cathode ray oscillograph were synchronized so that it was possible to measure the stress corresponding to each degree of strain. The peak stress and the maximum strain developed are given in Table VII for a range of four thicknesses of

TABLE VII
EFFECT OF THICKNESS OF RUBBER
(Test-piece, natural rubber tread)

Thick- ness (inch)	Energy input (foot-lb.)	Peak Stress (lb./sq. inch)	Max. strain (%)	$S^2/(I/V)$ (lb./sq. inch)	E , Av. modulus (lb./sq. inch)
$\frac{1}{8}$	21	420	119	700	290
$\frac{1}{4}$	8	400	80	830	530
$\frac{3}{8}$	7	455	69	620	450
$\frac{1}{2}$	4.4	540	92	690	380

natural rubber tread. After the stress producing this strain under impact had been accurately measured, similar test-pieces from the same batch were tested on the normal straight pull test.

The stress as measured under impact was applied in straight pull and the resulting deformation measured. This deformation corresponded within experimental error to the maximum strain results given in Table VII. It can, therefore, be concluded that no reduction in the deformation of the unit is caused by increasing the speed of testing from 1 inch per minute to that of the impact test.

Villars⁸ has recently reported that the modulus is almost independent of the elongation rate up to about 10 per cent per millisecond, which was in Villars' experiments the point at which the modulus began to increase. The authors' experience, however, suggests that with their form of test-piece (Villars used a dumbbell) the increase in modulus does not occur until elongation rates above 10 per cent per millisecond are attained. Experiments did not show any increase in modulus, and therefore the authors are unable to suggest a definite figure for the elongation rate at which this occurs.

The experimental conditions of the high-speed photography required that both stress and strain should be kept fairly small; hence only low energy inputs were used. These were chosen to give approximately the same peak stress for

all the samples; the results show that this was very nearly achieved for the first three samples. The values of $S^2/(I/V)$ show that the equation (using a constant modulus) is only approximately satisfied, as would be expected over a degree of strain of the order 100 per cent. The above results also were based on the first impact given to each specimen and therefore the breakdown of rubber structure is probably a complicating factor. However, to a first approximation the formula is valid within 20 per cent.

COMPARISON OF UNITS HAVING DIFFERENT SHAPES BUT CONSTANT VOLUME

As a further check on the validity or usefulness of the equation $I = S^2Al/2E$, units of four different shapes—cylinder, hollow cylinder, ellipse, and square—were tested. The test-piece dimensions in each case were:

Shape	Thickness (inch)	Area A (sq. inch)	Volume (cu. inch)
Square	0.5	1	0.5
Ellipse	0.5	1	0.5
Hollow cylinder	0.5	1	0.5
Cylinder	0.25	2	0.5

An existing A.S.T.M. disk mold was used to prepare all the above test-pieces and suitable two-piece metal inserts were made for the square and the ellipse. In the case of the hollow cylinder the end pieces of the disks were drilled and a metal rod was inserted and was removed after vulcanization. The cylinder test-pieces are normal A.S.T.M. test-pieces, with the thickness of rubber reduced to 0.25 inch. More accurate results would have been obtained by making special molds for the first three shapes, as some difficulties were experienced in maintaining adequate pressures for bonding, particularly with the hollow cylinder, but it is felt that the results in Table VIII, obtained with the above test-pieces, were sufficiently accurate to illustrate the present argument.

Apart from the cylinder, the agreement in the values for the stress is extremely good, and when it is realized that some of the test-pieces departed from

TABLE VIII
STRESSES DEVELOPED WITH TEST PIECES OF CONSTANT
VOLUME AND DIFFERENT SHAPES

(Energy input 50 foot-lb.)

No. of blows	Shape of cross-section			
	Square	Ellipse Stress (pounds per square inch)	Hollow cylinder	Cylinder
1	860	860	900	770
2	1000	990	1000	835
3	1040	1020	1070	910
4	1040	—	1100	920
5	1000	1000	1000	935
7	1070	1090	1920	900
10	1030	1030	1030	960
15	Broke	970	1020	900
17	at 12	—	1020	—
20		1000	Broke	865
25		Not broken	at 19	Not broken

the constant volume of 0.5 cubic inch by as much as 10 per cent, even the values obtained for the cylinder appear reasonable.

The multiple impact method¹ was used to evaluate the test-pieces of the four different shapes (Figure 9). The cylinder, ellipse, and square results are within experimental error. The low results obtained with the hollow cylinder are thought to be due to the difficulties in maintaining adequate molding pressures to give a good bond. If these results are compared with Figure 14 in the work of Buist and Naunton¹, it will be seen that, as indicated by the above equation, a fairly constant impact strength is obtained if the volume of rubber is maintained constant (irrespective of the shape), whereas if the volume of rubber is changed (see Figure 14 of the work of Buist and Naunton¹) the impact strength varies over a wide range.

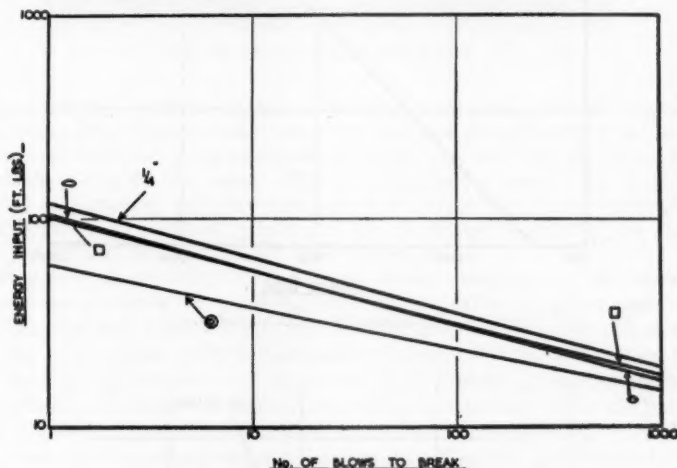


FIG. 9.—Multiple impacts on different shapes.

The present authors therefore feel that the equation given above can be regarded as a satisfactory first approximation.

However, the application of this equation may be examined one step further. In Figure 10 \sqrt{I} (where I = input energy) is plotted against the peak force for a large number of test-pieces made with natural rubber tread 0.25 inch thick. In these experiments the velocity at impact was not kept constant, as results from experiments where different weights were dropped from various heights were included. In view of the effect of filler structure described above, the peak force developed at the fifth successive blow has been used in constructing Figure 10. A reasonably good straight line can be drawn, but this line does not pass through the origin as it should if the equation applied exactly.

Similarly, the data available from the experiments with test-pieces of varying thickness have been plotted in Figure 11. In this case the square of the peak force has been plotted against the inverse of the length for three energy inputs of 40, 50, and 60 foot-pounds. The inexactness of the formula is shown by the departure of the curves from linearity.

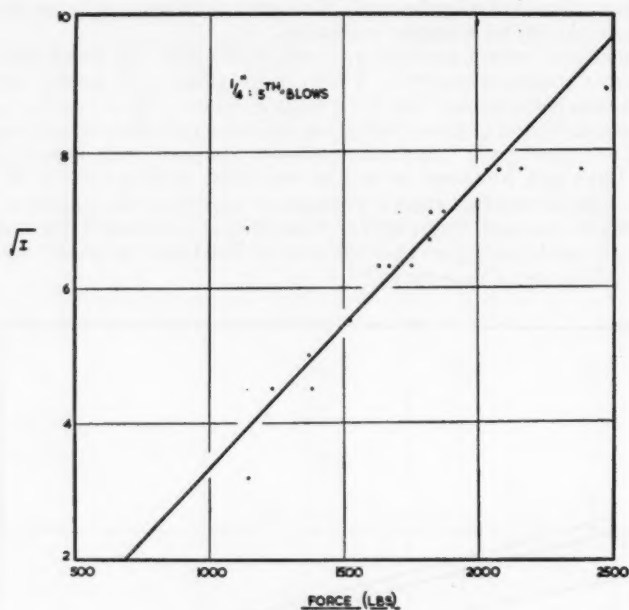


FIG. 10.—Variation of force with impact energy.

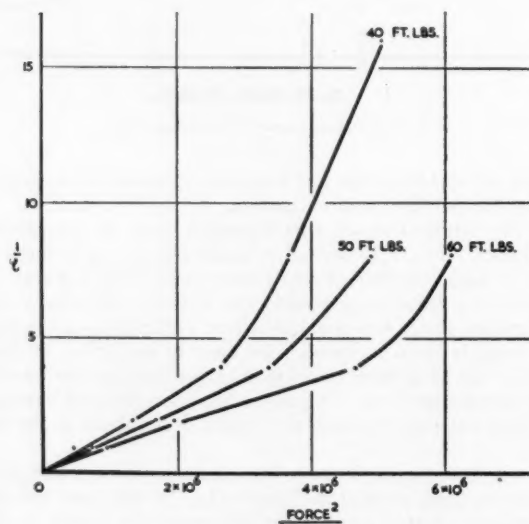


FIG. 11.—Variation of force with thickness.

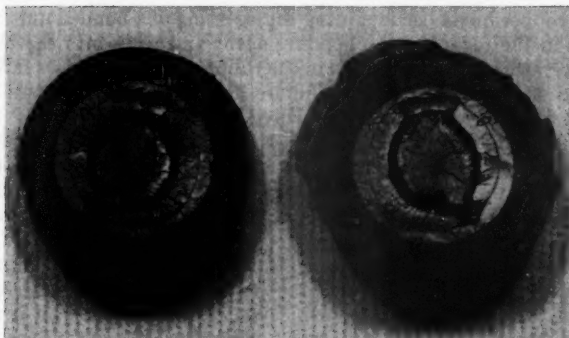


FIG. 12.—Three successive impact tears.

Figures 10 and 11 illustrate that, although the equation is a useful approximation, some other factors come into play, and one immediately looks to the Young's modulus term in the equation and postulates that any departure from the formula is due to this term. This is certainly the most likely source of error, but until further data are available it is impossible to state whether or not this is the only contributory factor to the discrepancies between the experimental results and those calculated from the equation.

Testing strength of rubber.—The normal tensile strength and tear strength measurements are useful for assessing whether the quality of a given compound is maintained or not, but neither tensile nor tear tests bear any definite relation to service. One reason for this discrepancy between normal and service tests is that the results obtained with the normal tests depend on the dimensions of the test-pieces. To assess the behavior of the product in service at the present time, it is essential that the strength of the rubber be measured on test-pieces having the same dimensions as the bonded units. The testing of bonded units, *e.g.*, by A.S.T.M. D 429, often reveals that failure occurs in the body of the rubber rather than in the region of the bonding agent. The optimum conditions for producing failure at the bonding agent have been stated above, and therefore it seemed logical to try to evolve a test method whereby failure would be produced in the rubber.



FIG. 13.—Minute tears under small blows.

When a rubber break occurs during the stressing of a bonded unit, the failure often starts in the region of the bonding agent and tears into the body of the rubber or begins from an initial flaw in the rubber. In both cases failure occurs by a process of tearing, and service failure in the majority of cases will be by tearing. A tear test was, therefore, evolved.

Standard A.S.T.M. bonded test-pieces with natural rubber tread 0.5 inch thick were held in a lathe, and a circular slit 6 mm. deep was cut in the rubber halfway between the two metal end pieces. These test pieces were then put in the falling-weight apparatus and subjected to successive blows of known energy input.

The method has the following features. The forces involved in propagating the initial cut can be measured. The area torn with each successive blow can be measured. As a known energy input is used for each blow, it is possible to calculate the energy involved in tearing. The effect of varying the energy input (and hence the stress) can be followed. It is possible to vary the mass of rubber from thin to thick sections and investigate the tearing of rubber having dimensions comparable to those of the service article.

No attempt is made to include quantitative data here, but the results obtained with the method are illustrated by some typical photographs.

Figure 12 shows the torn surfaces of a test-piece which has been subjected to three successive blows of an energy input of 80 foot-pounds. The area to be torn decreases with successive blows and the stress increases as a constant energy input is used.

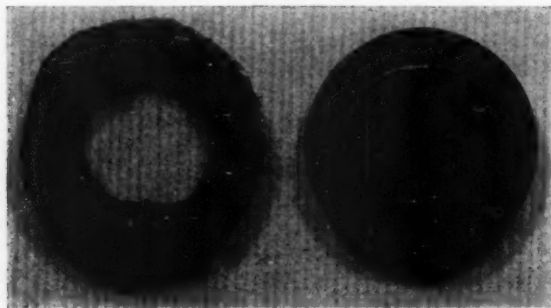


FIG. 14.—Change of direction of tear.

Figure 13 shows the torn surfaces of a test-piece which has been subjected to successive blows from a much lower energy input (5 to 10 foot-pounds). At these low energy levels the number of blows to produce rupture increases to the region of 250 to 400 for a natural rubber tread stock, and, as Figure 13 shows, a very small area of rubber is torn each time. It is impossible to make accurate measurements of the area torn in such cases, and experience so far indicates that the lower limit for the energy input should be such that tearing is complete within the first hundred blows. This leaves a wide latitude for investigating different energy levels.

Under certain conditions some compounds do not tear in such a way as to propagate the initial cut horizontally, but torn shear planes are formed in the body of the rubber until the tear has proceeded to one of the metal surfaces of

the end pieces. In Figure 14 such a test-piece is shown; the raised surface of the test-piece on the right is the part of the rubber which was bonded to the metal. A profile of this test-piece is shown in Figure 15; once again the distance the tear has traveled with each of the three successive blows is clearly indicated.

Many of the variables associated with this test method have still to be evaluated more systematically before the full potentialities of the method are known.



Fig. 15.—Profile of tear in Figure 14.

Although the method has been used in testing bonded units, there is no reason why it should not have a much wider application. The lack of correlation between tear tests (crescent, Delft, and angle) and service is due, among other reasons, to the fact that measurements are made on relatively thin test pieces and it is not permissible to extrapolate the results to thicker test pieces and hence to the performance of actual articles in service.

SUMMARY

The work was undertaken because no satisfactory and discriminating test is available for evaluating rubber-to-metal bonding agents. In former tests the testing of the bonding agent was confused with the testing of the test unit as a unit.

A method was evolved which discriminated between bonding agents which had previously been regarded as equivalent. In the course of the work new facts such as the importance of the volume of the rubber rather than the shape factor (which must, of course, be considered from the stability angle) came to light.

The significance of the work lies in two directions—better testing of metal-to-rubber bonding agents and a better understanding of the facts underlying the design of rubber-metal spring units. A tentative method for measuring the tear strength of the rubber used in the unit was put forward.

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RETRACTION TEST FOR SERVICEABILITY OF ELASTOMERS AT LOW TEMPERATURES *

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When the temperature is lowered, the flexibility of a polymer decreases as the second-order transition temperature is approached. The decrease in flexibility is caused by increased internal viscosity. This phenomenon is called the retarded elastic effect or viscoelastic effect. Additional decreased flexibility may be caused by first-order transition effects (crystallization) in polymers having a structure of sufficient regularity. When usefulness of elastomers at low temperatures is evaluated, both effects should be measured whenever possible.

A retraction test has been developed which rapidly gives a temperature index that correlates with the ultimate stiffness of elastomer vulcanizates at low temperatures. Ultimate stiffness includes increased modulus due to viscoelastic and first-order transition effects if present. The large deformation employed in this test (250 per cent elongation) causes rapid appearance of the stiffening due to crystallization in polymers having a regular structure. The test is based on the T-50 test¹. Various similar pieces of apparatus have been designed which yield the same type of data. Yerzley and Fraser² applied such a test to Neoprene and stated that it was inadequate. More recently, Svetlik³ applied a technique to the study of elastomers, using only 50 per cent test elongation. The test described in this paper uses 250 per cent initial elongation and differs from other tests also in the method of analyzing the data.

APPARATUS AND TESTING METHOD

The retraction tester consists of an apparatus that permits the measurement of the elongation of 2-inch T-50 samples⁴ (60-gage) at all times during a run. The front view in Figure 1 shows the holder with the samples inserted; three of the samples are unstretched and three are stretched ready for insertion in the cooling bath. Wire leads (piano wire), attached to the samples by means of hooks, pass through binding posts which permit the samples to be anchored at any elongation. Strings attached to the ends of the wire leads pass over small pulleys at the top of the instrument. The free ends of the string are attached to small counterweights. A scale graduated in 0.1 inch is inserted behind the leads. Attached to the leads are disk-shaped indicators to enable the length of the sample to be read.

The overall view in Figure 1 shows the apparatus standing in an unsilvered Dewar flask in a wooden frame. This frame, which was built to act as a convenient stand for the apparatus and additional insulation, is filled with glass wool and held in place with a sheet of polyethylene. A window in the frame

* Reprinted from *Analytical Chemistry*, Vol. 23, No. 2, pages 322-327, February 1951. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its International Meeting in Cleveland, Ohio, October 11-13, 1950.

permits reading a totally immersed thermometer. The Dewar flask contains a stirrer and a heating element connected to the house current through an autotransformer to maintain a proper heating rate.

The procedure is based on the background material described in the following sections. A 2-inch T-50 sample (60-gage) of the vulcanizate under test is

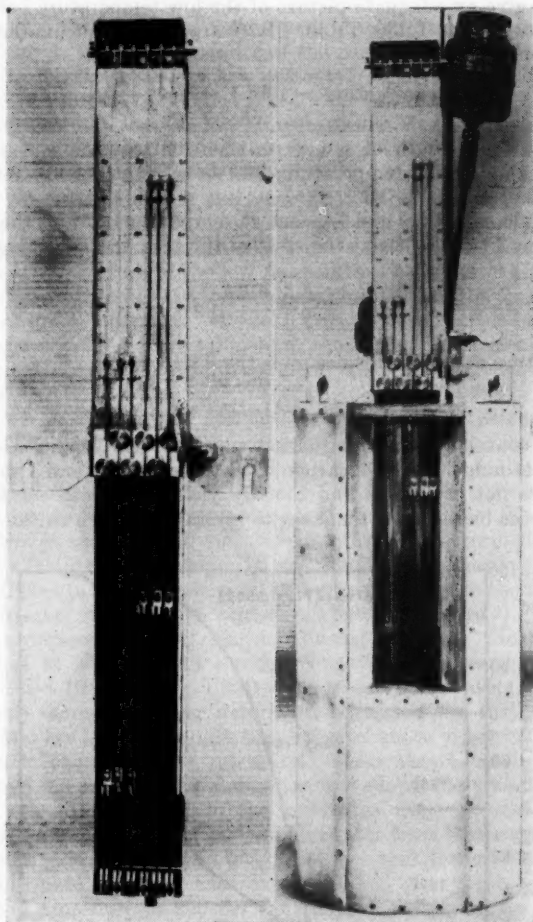


FIG. 1.—Retraction apparatus. *Left.* Sample holder. *Right.* Overall view.

placed in the hooks, stretched 250 per cent (from 2 to 7 inches), and locked in the stretched position by turning the thumb nut on the binding post. The rack containing the stretched samples is placed in a methanol bath, which had been cooled to -70°C by dipping into it dry ice contained in a cylindrical wire cage. The stretched samples are conditioned for 10 minutes. The thumb nuts

are released, allowing the samples to retract freely. The temperature of the bath is then raised 1°C per minute by means of the heating coil. The length of each sample is measured at 2° intervals. The bath is agitated throughout the test.

The temperatures at which the sample retracts 10, 30, 50, and 70 per cent of the original elongation are called TR10, TR30, TR50, and TR70, respectively. These values give an adequate picture of the low temperature behavior. Retraction values (TR10, TR30, TR50, TR70) are computed from the data by the following formula:

$$\% \text{ retraction} = 100 \left(1 - \frac{L_T - L_0}{L_s - L_0} \right)$$

where L_s = overall length of sample in stretched condition at start of test, L_T = length at observed temperature, and L_0 = length in unstretched condition.

For example, when L_T is 6.5 inches at temperature T and the sample was stretched from 2 to 7 inches at the start of the test, the percentage retraction equals:

$$100 \left(1 - \frac{6.5 - 2}{7.0 - 2} \right) \text{ or } 10\%$$

The temperature at which this occurs is the TR10 value.

TYPICAL DATA

Figure 2 contains typical retraction curves of Hevea and GR-S 10 vulcanizates containing 50 parts of carbon black, accelerators, and 2 parts of sulfur. GR-S 10 does not crystallize and thereby yields a smooth retraction curve. However, Hevea has a strong tendency to crystallize, which causes an irregular

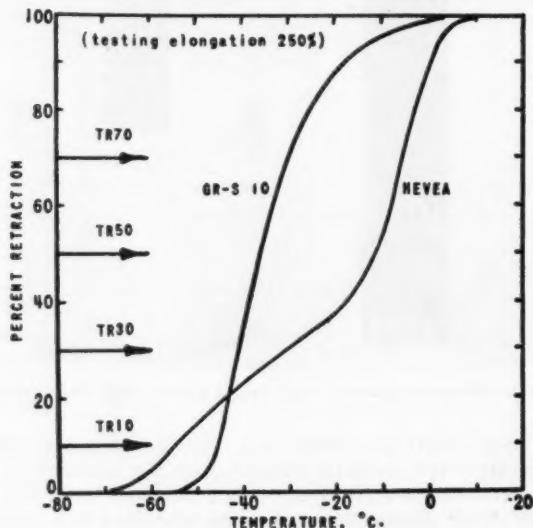


FIG. 2.—Typical retraction data on GR-S 10 and Hevea.

TABLE I

RETRACTION VALUES OF GR-S 10 AND HEVEA FROM CURVES IN FIGURE 1

	TR10	TR30	TR50	TR70
GR-S 10(° C)	-45.4	-40.3	-35.5	-28.7
Hevea (° C)	-54.2	-29.2	-11.1	-5.0

retraction curve. The retraction values were obtained from these curves and recorded in Table I. In the remainder of the paper retraction curves are not given; only the retraction values are presented—that is, the TR10, TR30, TR50, and TR70 values.

The TR10 value indicates the low temperature merit of the elastomer prior to low temperature storage. In this respect, this value is similar to the T_{10} value⁶ obtained when using the torsion modulus test. This measurement is influenced by viscoelastic effects and very little by crystallization. Because crystallization does influence low temperature properties greatly, especially after low temperature storage, additional criteria such as TR70 must be used to obtain a complete picture of the low temperature behavior of elastomers.

The TR70 value indicates the low temperature merit of the elastomer after a long period of low temperature storage. This measurement is influenced by both viscoelastic effects and crystallization, thereby giving a measure of ultimate stiffness. Hevea has a TR70 value of -5.0°C , and GR-S 10 has a TR60 value of -28.7°C . This indicates that, on storage at low temperatures, Hevea would eventually become less flexible than GR-S 10, especially under static stress. Thus, higher cold compression set was found for Hevea than for GR-S 10.

Effect of elongation on retraction values.—The sample is purposely given a large deformation to induce rapid crystallization on cooling. The retraction values of the Hevea and GR-S 10 vulcanizates previously described were measured at various testing elongations. It was found that increasing the testing elongation of Hevea (above 100 per cent) caused a sharp rise in the TR70 value, which begins to level off at 200 per cent elongation (see Figure 3). This rise is caused by the presence of crystallization during the test. Near maximum effect is reached at 250 per cent testing elongation. Increasing the testing elongation of GR-S 10 causes the TR70 value to decrease sharply until 200 per cent is reached; thereafter larger deformations cause little further decrease. The TR10 values are influenced only slightly by changes in testing elongation.

Because little change in the retraction values occurs on increasing the elongation above 250 per cent, this elongation was adopted as standard. Many experimental vulcanizates break in the apparatus when greater elongations are used. Using 250 per cent elongation is desirable from that standpoint also.

Testing Hevea gum stocks.—The use of 250 per cent testing elongation has been found adequate in every case except Hevea gum vulcanizates. The standard testing procedure of 250 per cent testing elongation for Hevea vulcanizates containing less than 40 parts of carbon black gives misleading results. Figure 4 shows data on the effect of both testing elongation and concentration of carbon black on TR70. Using 250 per cent testing elongation for a pure gum Hevea gave a TR70 of -56.8°C , whereas a testing elongation of 400 per cent gave a TR70 of -1.8°C . Therefore, elongations of 400 per cent should be used for Hevea gum stocks.

Effect of low temperature storage upon TR70.—Normally, compounded Hevea crystallizes slowly. When the storage temperature is varied from the

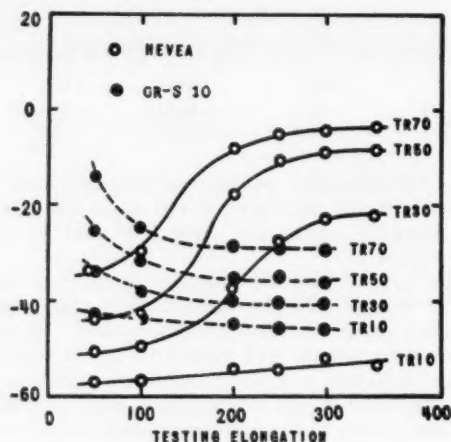


FIG. 3.—Effect of testing elongation on retraction values.

optimum, -25°C , crystallization may appear more slowly. The same effect occurs in GR-S elastomers having low styrene content when polymerized at low temperatures; the optimum for such elastomers is close to -45°C . It is also known that the application of stress to a sample increases the rate of crystallization. The result of these tendencies depends on the selected storage temperature and degree of stress imposed on the sample. Under the conditions of this test crystallization appears rapidly.

It is believed that 250 per cent testing elongation creates a condition which induces nearly maximum crystallization during the short time of the test. This

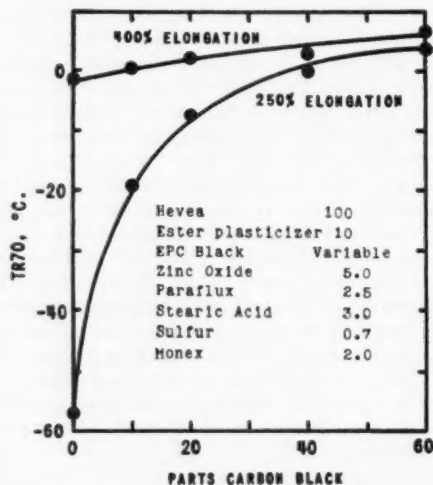


FIG. 4.—Effect of carbon black on TR70 of Hevea vulcanizates.

was verified by storing the retraction samples at 250 per cent elongation at -55°C . Without warming them, the samples were plunged to -70°C in the retraction bath placed in the cold box, and a subsequent run was made. The TR70 determined by this procedure and the normal procedure is compared in Table II. If storage at low temperature has increased the crystallization in a

TABLE II
EFFECT OF STORAGE AT -55°C ON TR70 OF VULCANIZATES OF ELASTOMERS

Polymer	Time of storage (hours)	Storage temperature ($^{\circ}\text{C}$)	TR70 ($^{\circ}\text{C}$)
Hevea	0		-5.4
	71	-55	-4.0
GR-S 10	0		-29.8
	73	-55	-29.7
B/S, 90/10, 41°F	0		-30.4
	73	-55	-29.1
Polybutadiene, 41°F	0		-17.0
	73	-55	-15.0
Polybutadiene, 77°F	0		-34.1
	72	-55	-32.4

sample, its TR70 should be at a higher temperature. Only small changes due to storage were observed. The magnitude of the change in TR70 due to storage is close to the accuracy of the test. Therefore, these changes are not considered significant, but they are indicative of the high degree of crystallinity obtained in this test.

The retraction values for several standard elastomers are contained in Table III. The TR10 values indicate that Hevea and Butyl are the most flexible materials at low temperatures when no storage is encountered. The order of merit as described by TR10 would be polybutadiene (41°F), GR-I, Hevea, GR-S 10, GR-S (41°F), Neoprene, and Paracril. However, if each

TABLE III
RETRACTION VALUES OF STANDARD ELASTOMERS
($^{\circ}\text{C}$)

Rubber	TR10	TR30	TR50	TR70
GR-S 10	-45.4	-40.3	-35.5	-28.7
GR-S (41°F)	-45.1	-40.2	-43.8	-27.8
GR-I	-54.3	-41.8	-31.9	-23.7
Polybutadiene (41°F)	-59.9	-41.3	-29.3	-21.8
Paracril 26 NS90	-27.5	-22.5	-17.8	-12.0
Hevea	-54.2	-29.6	-11.1	-5.0
Neoprene	-40.4	-35.2	-24.6	+3.6

Compounded with 50 parts of black, using standard curing methods.

material is stored at low temperatures to allow crystallization to take place, the flexibility of polybutadiene (41°F), Hevea, and Neoprene would be greatly reduced, and the order of merit would become: GR-S 10, GR-S (51°F), GR-I, polybutadiene (41°F), Paracril, Hevea, and Neoprene as indicated by the TR70 values.

LOW TEMPERATURE FLEXIBILITY OF BUTADIENE-STYRENE POLYMERS

The TR70 of several polybutadiene vulcanizates made at various temperatures has been measured. Table IV contains the vulcanization details. It was found that decreasing the temperature of polymerization caused the TR70 to rise (see Figure 5). Decreasing the temperature of polymerization from 122° to 0° F raised the TR70 from -45.4° to -8.9° C. This change can be explained by understanding the accompanying structural changes. Hart and

TABLE IV
TYPE FORMULA

Polymer	100
EPC channel black	50
Zinc oxide	5
Paraflux	5
Stearic acid	1.5
Sulfur	2.0 ^a
MBT ^b	1.5
DPG ^c	0.4 ^d

Cure 45 minutes at 292° F

^a Except where otherwise specified.

^b Mercaptobenzothiazole.

^c Diphenylguanidine.

^d Varied to equalize rate of cure.

Meyer⁶ found by infrared absorption studies that the temperature of polymerization increased the structural regularity, as predicted through x-ray analysis by Beu, Reynolds, Fryling, and Murry⁷ and through dilatometer work by Lucas⁸. Some dilatometer data obtained at the General Laboratories are presented in Figure 5. It may be assumed that the decrease in volume accompanying low temperature storage is due to crystallization and this decrease is a measure of the crystallization. It can be easily seen that increasing crystallization due to low temperature polymerization raises the retraction value TR70.

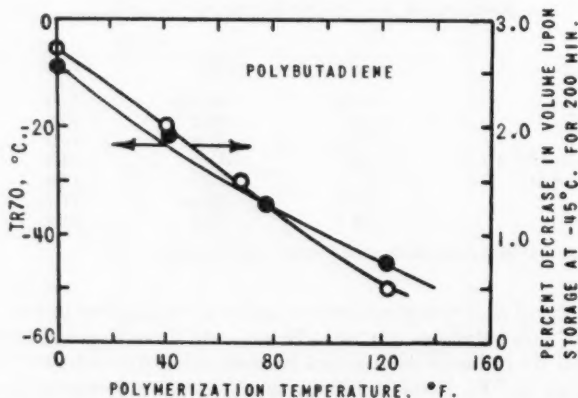


Fig. 5.—Effect of polymerization temperature on TR70 and extent of crystallization for polybutadiene.

Copolymerization of butadiene with comonomers having high second-order transition temperatures generally results in polymers having poorer low temperature properties. Figure 6 contains a plot of TR70 against the styrene content in vulcanizates of butadiene-styrene copolymers made at 41° F. The compounding formula is presented in Table IV. Figure 6 shows that increasing the styrene content to 15 or 20 parts actually improves the ultimate flexibility of the vulcanizates at low temperatures. Even a polymer containing 29 per cent styrene has a lower TR70 than polybutadiene. These apparent discrepancies can be explained by determining the crystallization in these polymers. These results are also presented in Figure 6. The addition of 15 parts of styrene as a comonomer reduces the crystallization to a very low quantity for 41° F copolymers. Here the decrease in volume with storage at -45° C is almost negligible. Reducing crystallization by introducing a comonomer, styrene, improves the TR70 despite the rise in second-order transition temperature which accompanies this procedure.

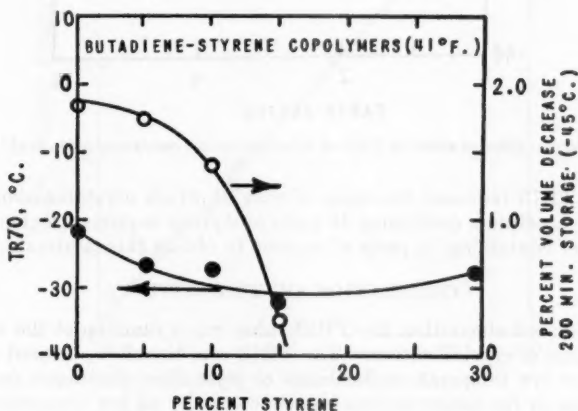


FIG. 6.—Effect of styrene on TR70 and extent of crystallization.

Usually ultimate stiffness is difficult to measure using ordinary test methods, because increasing the comonomer not only decreases the amount of crystallization but also decreases the rate at which it appears. This effect is exaggerated when the polymer is in the compounded condition. The cure in these polymers produces large effects upon their low temperature characteristics. Figure 7 contains the TR70 values of vulcanizates of butadiene-styrene copolymers made at 41° F with various states of cure. The compounding formula is contained in Table IV. A sharp improvement is noted in the low temperature properties, as indicated by TR70 values of polybutadiene with increasing cure. However, increasing cure for GR-S (29 per cent styrene) made at 41° F produces vulcanizates of poorer low temperature flexibility. Increasing cure reduces crystallization, thereby improving the TR70 of polybutadiene, and also reduces flexibility owing to the increased number of sulfur cross links. Because there is no crystallization in GR-S made at 41° F, increasing cure produces poorer TR70 values. The plot of TR70 versus cure shows a minimum for a polymer having an intermediate styrene content. The

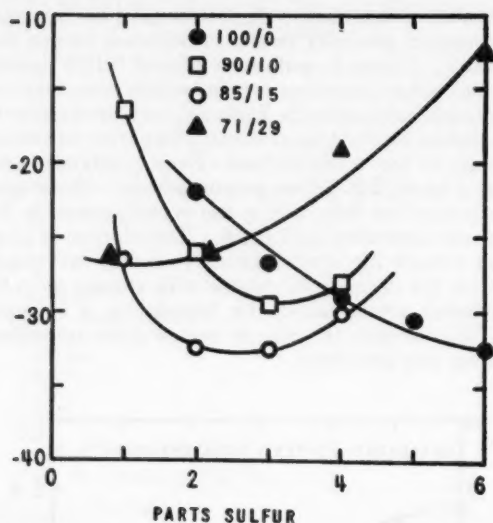


Fig. 7.—Effect of sulfur on TR70 of butadiene-styrene copolymers made at 41° F.

minimum TR70 indicates the state of cure at which crystallization has been arrested. A polymer containing 10 parts of styrene requires a higher cure than the polymer containing 15 parts of styrene to obtain this minimum.

CORRELATION OF TR10 WITH T_{10}

It was stated above that the TR10 value was a function of the viscoelastic effect but not of crystallization. The TR10 can, therefore, be used as a figure of merit for low temperature flexibility of crystalline elastomers for dynamic applications, or for noncrystalline elastomers under all low temperature conditions. This figure of merit is similar to the T_{10} value obtained when testing low temperature flexibility with a torsion modulus apparatus.

TABLE V
TYPE FORMULA

	A	B*
Polymer	100	100
EPC black	50	50
Zinc oxide	5	5
Paraflux	5	—
Stearic acid	1.5	1.5
Sulfur	2	1-2
MBT ^b	1.5	—
DPG ^c	0.4 ^d	—
MBTS ^e	—	1.5

Cure 45 minutes at 292° F

* Used exclusively for polymers containing acrylonitrile.

^b Mercaptobenzothiazole.

^c Diphenylguanidine.

^d Varied to equalize cure.

^e Mercaptobenzothiazyl disulfide.

The TR10 and T_{10} values were measured for vulcanizates of butadiene-isoprene, butadiene-styrene, butadiene-acrylonitrile, and butadiene-isoprene-acrylonitrile. Because exact knowledge of the composition of these elastomers is not essential to the understanding of the test, this information has not been included. Table V contains compounding data. Formula A was used for butadiene-isoprene and butadiene-styrene, whereas Formula B was used exclusively for polymers containing acrylonitrile. In Figure 8 is a plot of the TR10 value versus the T_{10} value of these vulcanizates. The points form a straight line. The order of low temperature merit of the polymers given by the TR10 is therefore similar to that given by T_{10} .

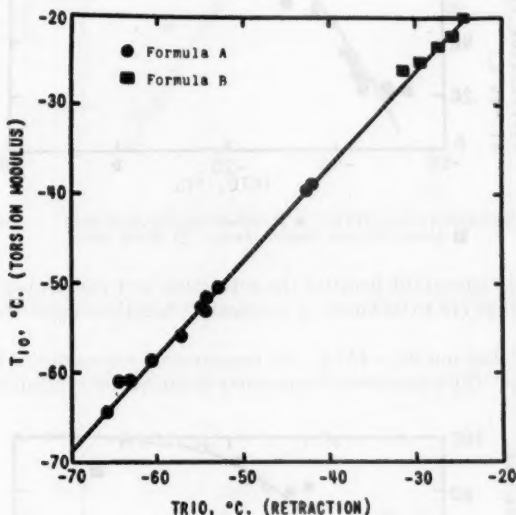


Fig. 8.— T_{10} vs. TR10 of butadiene-styrene, butadiene-isoprene, and butadiene-acrylonitrile vulcanizates.

This correlation of TR10 with T_{10} is more general than is indicated in Figure 8. In addition to the polymers mentioned above, Hevea, polyisoprene, terpolymers of butadiene and isoprene with styrene, aryl acrylates, and vinylpyridine also have the same correlation. Variation of sulfur from 1 to 5 parts, addition of plasticizers (ester or hydrocarbon), and changes in carbon black content do not alter the relationship. It is believed, therefore, that the TR10 can be used reliably as a measure of the low temperature flexibility of elastomer vulcanizates where low temperature storage is not encountered and for non-crystalline vulcanizates.

TR70 AS A MEASURE OF COMPRESSION SET

Both TR70 and compression set (measured according to Navy Department Specifications 33-R-9) were measured on a series of experimental stocks, which contained 15 parts of ester plasticizer and 40 parts of Philblack O. It was found that the TR70 could be used as an index of compression set, because stocks

having equal TR70 values have equal compression set values. Naturally, as the TR70 values decrease the compression set values also decrease.

If the TR70 of these stocks is plotted against their compression set (at -35° and -45° C), smooth curves are developed (see Figures 9 and 10). The retraction test can now be used to estimate the compression set of vulcanizates.

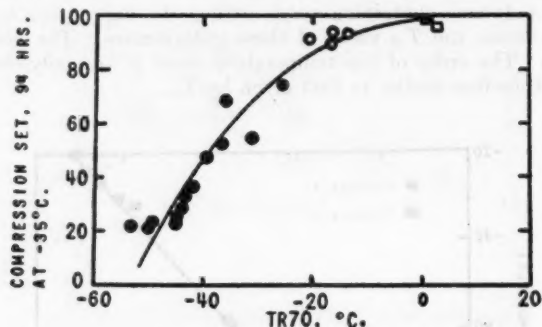


Fig. 9.—Compression set vs. TR70. ● Butadiene-styrene copolymers ○ Perbunan. ■ Hevea (50 parts channel black). □ Hevea (gum).

This function is important because the retraction test can be performed in 45 minutes. Storage (48 to 96 hours) is necessary when the compression set values are measured.

At -35° C, but not at -45° C, the compression set values of Hevea stocks lie on the curve. This apparent discrepancy is caused by crystallization, which

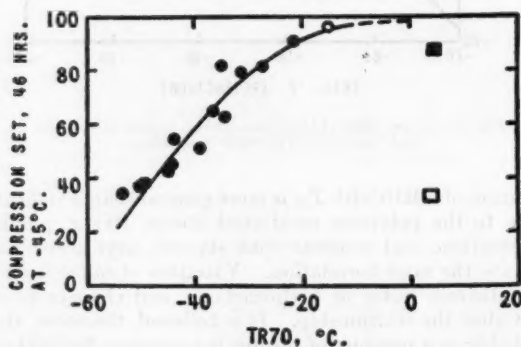


Fig. 10.—Compression set vs. TR70. ● Butadiene-styrene copolymers. ○ Perbunan. ■ Hevea (50 parts channel black). □ Hevea (gum).

takes place less rapidly at -45° than at -35° C. Under the conditions of the compression set test, apparently maximum crystallization was not obtained at -45° C. Hevea stocks therefore, when stored at -45° C for 96 hours, yield compression set values that are too low. If the storage time of the compression set test were increased sufficiently, the compression set values would eventually rise to the value indicated by its TR70 in Figure 10.

CORRELATION OF TR70 WITH HARDENING IN COLD STORAGE

TR70 has also been correlated with hardening in cold storage (Figures 11 and 12). Both tread stocks containing 50 parts of easy processing carbon black and 2 parts of sulfur and gasket stocks containing 15 parts of ester plasticizer, 40 parts of Philblack O, and 0.7 parts of sulfur were included in this correlation.

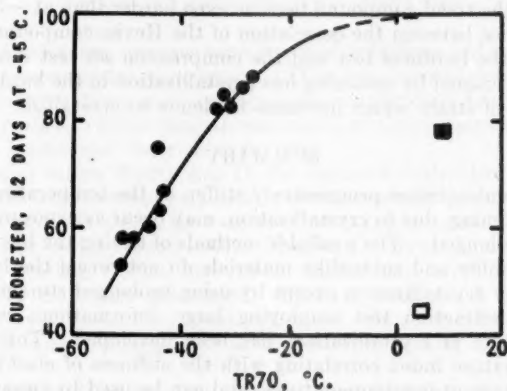


FIG. 11.—Hardness after storage at -45°C vs. TR70. ● Butadiene-isoprene-styrene copolymers and terpolymers. ■ Hevea (50 parts channel black). □ Hevea (gum).

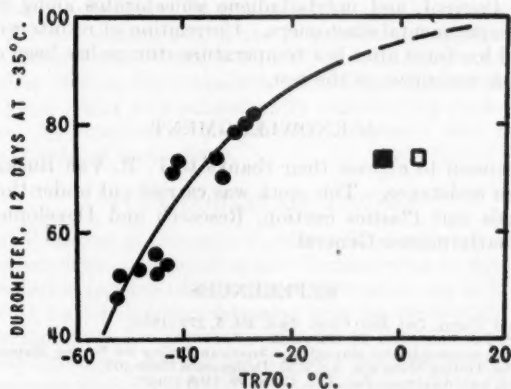


FIG. 12.—Hardness after storage at -35°C vs. TR70. ● Butadiene-isoprene-styrene co- and terpolymers. ■ Hevea (50 parts channel black). □ Hevea (gum).

Most of the stocks were based on butadiene-styrene copolymers polymerized at 41° and 122°F , respectively, and contained various proportions of styrene. Tread stocks based on Hevea, butadiene-isoprene copolymers, butadiene-isoprene-styrene terpolymer, and a gasket stock containing no black based on Hevea were included. Durometers were measured at intervals over 12-day periods at -35° and -45°C , respectively. Hardness of all the stocks with

the exception of the Hevea stocks correlated fairly well with TR70 at both -35° and -45° C.

Hardness of the Hevea stocks did not correlate with TR70 at either temperature. The smoked sheet tread compound attained approximately equivalent hardness at -35° and -45° C. The smoked sheet gasket compound was about as hard as the tread compound when stored for 12 days at -35° C, but when stored for a similar period at -45° C the gasket compound hardened very little, whereas the tread compound became even harder than at -35° C.

The difference between the correlation of the Hevea compound with TR70 at -35° C in the hardness test and the compression set test discussed previously can be explained by assuming less crystallization in the hardness test due to the absence of strain which increases tendency to crystallize.

SUMMARY

Elastomer vulcanizates progressively stiffen as the temperature is lowered. Additional stiffening, due to crystallization, may occur as exposure to low temperatures is prolonged. The available methods of testing the low temperature flexibility of rubber and rubberlike materials do not reveal the losses in flexibility caused by crystallization except by using prolonged storage at low temperatures. A retraction test employing large deformations, which greatly increases the rate of crystallization, has been developed. This test rapidly gives a temperature index correlating with the stiffness of elastomer vulcanizates after storage at low temperatures, and can be used to measure the merit for low temperature applications of both crystallizable and noncrystallizable elastomers. This test in conjunction with conventional (room temperature) tests has been used successfully to study the low temperature performance of Hevea, GR-S, Paracril, and polybutadiene vulcanizates along with vulcanizates of many experimental elastomers. Correlation of results with cold compression set and hardness after low temperature storage has been excellent and substantiates the usefulness of the test.

ACKNOWLEDGMENT

The authors wish to express their thanks to P. R. Van Buskirk and A. S. Weisser for their assistance. This work was carried out under the sponsorship of the Chemicals and Plastics Section, Research and Development Branch, Office of the Quartermaster General.

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BUTADIENE-STYRENE RESINOUS COPOLYMERS *

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In the past five years, resinous copolymers of butadiene and styrene have become of great commercial importance. This development has been spurred by the availability of these monomers in large quantities and at low prices as a result of the synthetic rubber program sponsored by the Government in cooperation with the rubber and chemical industries.

In the period before World War II, the rubber industry had become interested in resinous copolymers, particularly those obtained by chemical reactions of natural rubber. At that time such products as chlorinated rubber (Parlon, Hercules Powder Co.), cyclized rubber (Pliolite, Goodyear Tire & Rubber Co., and Marbon, Marbon Corp.), and rubber hydrochloride (Pliofilm, Goodyear Tire & Rubber Co.) were developed. Cyclized rubber has been of special interest as a rubber reinforcing agent and as the vehicle or binder for pigments in special protective coatings, such as concrete paints and corrosion-resistant coatings.

These promising developments, however, were cut short by the war, during which a large portion of the research and development effort of the rubber industry was channeled into the synthetic rubber program. It was recognized, however, that butadiene and styrene could be used to make resinous copolymers as well as rubbery copolymers, by proper selection of the charging ratio of the monomers. The first description of the properties and applications of a commercially available resin (Pliolite S-3, a 15/85 butadiene-styrene copolymer) was published in 1946 as the outgrowth of work by Borders, Juve, and Hess¹. Other high-styrene resins were subsequently described by Jones and Pratt² and Fox³. General information on high-styrene polymers was summarized by Winkelmann⁴, Fordyce⁵, and others⁶.

POLYMERIZATION STUDIES

The patent literature of the early thirties is filled with references to butadiene-styrene copolymers, as a result of the German work to develop Buna synthetic rubbers, but as early as 1930 scattered⁷ references can be found to German and British work on copolymers containing large amounts of styrene and small amounts of butadiene. No particular effort was made at that time to commercialize these findings. Konrad and Ludwig⁸ prepared emulsion copolymers of butadiene-styrene containing 47.5 to 70 per cent styrene, but were more interested in the rubberlike properties of the products. A recent patent⁹ claimed copolymers of butadiene and styrene containing 80 to 95 per cent styrene. Smith¹⁰ claimed a waterproof coating consisting of a high styrene-low butadiene copolymer admixed with polyisobutylene and a waxlike material. Sparks and coworkers¹¹ claimed that electrical insulating compositions of high-styrene

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 319-324, February 1951. This paper was presented at the International Meeting of the Division of Rubber Chemistry of the American Chemical Society, Cleveland, Ohio, October 11-13, 1950. The greater portion of the paper was presented first at the Rubber Chemistry Division meeting of the Chemical Institute of Canada at Toronto, June 21, 1950.

resins and polyisobutylene were of particular value in the construction of ultra-high-frequency radio transmitting and receiving systems. Te Grotenhuis¹² mixed a relatively tough butadiene-styrene in latex form with a well modified butadiene-styrene copolymer and isolated the product by co-coagulation. A blend suitable for shoe soles, wire covering, etc., was claimed¹³ by mixing GR-S with 25 to 100 parts of a high styrene-low butadiene resin (5 to 30 per cent) butadiene content and 10 to 25 parts of a cellulosic floc.

Comparatively little information on polymerization processes leading to high-styrene resins can be found in the scientific literature. MacLean, Morton, and Nichols¹⁴ recently studied butadiene-styrene copolymers through the entire range of monomer composition. By the use of *tert*-hexadecyl mercaptan (hexadecanethiol) as modifier and isolation of polymer at low conversion, products of relatively narrow range of molecular weight and relatively homogeneous as to comonomer composition of the chains were obtained. Meehan¹⁵ and Koningsberger and Salomon¹⁶ also studied butadiene-styrene copolymers of various ratios. Mitchell and Williams¹⁷ recently completed an excellent laboratory study of high styrene-low butadiene copolymers, and observed that the polymerization characteristics were similar to those found with GR-S, although by no means identical.

PREPARATION OF BUTADIENE-STYRENE RESINOUS COPOLYMERS

It was considered of interest to prepare under carefully controlled laboratory conditions a series of butadiene-styrene copolymers with charging ratios of 50/50, 40/60, 30/70, 20/80, and 10/90. Polystyrene was prepared under the same conditions as a control.

The polymerization recipe employed was of the GR-S type, as shown in Tables I and II.

A stock solution of sodium myristate was prepared from Neofat 13 (technical myristic acid, Armour & Co.) and used for all the polymerizations. The ingredients were measured into a 1-quart beverage bottle, with a monomer charge of 180 grams, closed with a cap having a Chemigum sealer and Teflon gasket, and rotated at 30 r.p.m. in a water bath maintained at 50° C. After an appropriate time the bottle was pressured with nitrogen and a syringe sample was removed for determination of solids content. After reaction was substantially complete, the contents of the bottles were blended and a portion was set aside for determination of latex properties. Then Wingstay-S (Goodyear Tire & Rubber Co.), a nonstaining antioxidant, or phenyl-2-naphthylamine (PBNA), was added to the remaining latex, which was coagulated with dilute hydrochloric acid. The product was washed free of chloride ion in a centrifuge and vacuum-dried at 50° C.

TABLE I
PREPARATION OF BUTADIENE-STYRENE COPOLYMERS AT 50° C^a

	1	2	3	4	5	6
Butadiene	0	10	20	30	40	50
Styrene	100	90	80	70	60	50
Dodecanethiol	0.10	0.15	0.20	0.25	0.30	0.35
Polymerization time (hours)	17	19.5	19.5	20	20	20.5
Total solids (%)	35.8	36.0	35.9	36.2	36.6	36.0
Conversion (%)	97.0	97.5	92.7	98.0	99.0	97.5
pH of latex	10.45	10.2	10.1	10.0	9.8	9.65

^a Recipe. Water, 180 parts; monomers, 100 parts; sodium myristate, 5 parts; potassium persulfate, 0.3 part. 1.5 parts of Wingstay S added to each latex before coagulation.

TABLE II
PREPARATION OF MORE HIGHLY MODIFIED BUTADIENE-STYRENE
COPOLYMERS AT 50° C^a

Sample no.	Butadiene (%)	Dodecane-thiol	Polymerization (Hours)	Total solids (%)	Conversion (%)
7	0	0.15	18	36.9	99.5
8	0	0.20	18	37.2	100
9	0	0.25	18	36.9	99.5
10	10	0.20	18	37.2	100
11	10	0.25	18	37.2	100
12	10	0.30	18	37.2	100
13	20	0.30	18	37.2	100
14	20	0.35	18	37.2	100
15	20	0.40	18	36.7	98.8
16	30	0.40	20	37.2	100
17	30	0.45	20	36.9	99.5
18	30	0.50	20	37.8	99.0
19	40	0.50	20	37.2	100
20	40	0.60	20	36.5	98.0
21	50	0.50	20	36.6	98.5
22	50	0.55	20	37.2	100
23	50	0.60	20	37.2	100

^a Recipe. Water, 180 parts; monomers, 100 parts; sodium myristate, 5 parts; potassium persulfate, 0.3 part. One part of PBNA added to each latex before coagulation.

No special study was made of changes occurring during polymerization, because the objective was to carry each polymerization to substantial completion. The amount of thiol modifier was increased in proportion to the amount of butadiene employed (Table I). To obtain significant flow tests, another series of more highly modified resins was prepared (Table II). The reaction time required to attain 97 to 99 per cent conversion gradually increased as the ratio of butadiene charged was increased. The pH of the latex as obtained from the reactor exhibited a small but regular decrease with increasing butadiene content, but no ready explanation for this is available.

BUTADIENE-STYRENE COPOLYMER LATEXES

The latex samples were diluted to 30 per cent solids content, vacuum-stripped free of monomers and other volatile impurities (maximum temperature 50° to 60° C) and diluted again to 30 per cent solids. Table III summarizes the properties determined on these samples. The pH values on the copolymer samples were practically constant, whereas the polystyrene latex exhibited a somewhat higher value. The Brookfield viscosities were uniformly low and independent of the spindle speed employed (2, 4, 10, and 20 r.p.m.), thus indicating lack of thixotropy. Surface tension values were fairly constant, but tended to increase with increasing butadiene content. This behavior probably is related to the pH values. The soap requirement and turbidity measurements¹⁸ indicated that the average latex particle size decreased with increasing butadiene content, but the overall change was small. In comparison, Type II GR-S latex gives values in the same range covered by these experimental latices.

The mechanical stability of the latex varied greatly with copolymer composition. Polystyrene and the 10/90 butadiene-styrene copolymer exhibited a high degree of mechanical stability, the 20/80 and 30/70 copolymers a moderate degree, and the 40/60 and 50/50 copolymers a low degree of stability. The

TABLE III
PROPERTIES OF BUTADIENE-STYRENE COPOLYMER LATICES^a

	1	2	3	4	5	6
B-S charge ratio	0/100	10/90	20/80	30/70	40/60	50/50
Brookfield viscosity (cp.)	20	20	20	20	20	20
pH	10.32	9.93	9.88	9.88	9.88	9.88
Surface tension (dynes/cm.)	55.0	55.5	55.2	58.0	58.2	59.0
Soap requirement (%) ^b	4.8	4.9	5.6	6.2	7.15	7.25
Turbidity ^c	0.29	0.30	0.28	0.25	0.24	0.19
Mechanical stability ^d (sec.)	>40 min.	>40 min.	40	30	<30	<30
Film formation at room temperature	Flakes easily	Flakes	Checks	Tough	Rubbery	Soft, rubbery
Chemical stability (salt) ^e	0.323	0.306	0.302	0.63	> 0.8	> 0.8
Coagulation (salt) ^f	1.60	1.50	1.45	5.65	>13.5	>13.5

^a Properties determined on stripped latices at 30% solids.

^{b, c} See Reference 18.

^d See Reference 19.

^e Chemical stability = $\frac{\text{ml. of 1 } M \text{ NaCl solution}}{\text{ml. of latex} + \text{ml. of 1 } M \text{ NaCl solution}}$

^f Millimoles of NaCl per gram of polymer for complete coagulation.

differences are so great that it must be concluded that polymer composition is capable of exerting a specific effect upon the mechanical stability of the corresponding latex. On the other hand, the chemical stability of these latexes on addition of 1 *M* sodium chloride solution increased markedly as the butadiene content of the polymer was increased. The end point was taken as the point at which the small discrete particles, formed on initial addition of the salt solution, suddenly lumped together in one mass. Whereas polystyrene and copolymers of low butadiene content were completely coagulated by the addition of only 1 to 2 millimoles of salt per gram of polymer, copolymers of higher

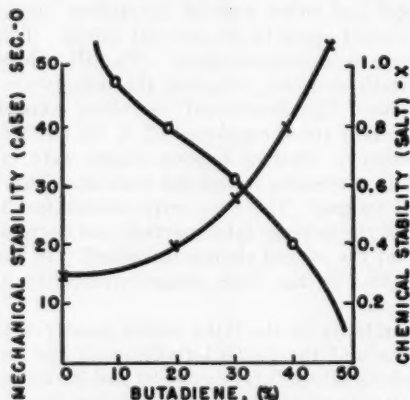


FIG. 1.—Latex stability vs. butadiene content.

butadiene content were not completely coagulated with more than 13.5 millimoles of salt. The mechanical and chemical stability data are plotted in Figure 1 as a function of butadiene content. Mechanical and chemical stabilities were also determined on latexes 7 through 23 to confirm the results given in Figure 1.

Films were cast from each latex for examination of their properties. Polystyrene and the 10/90 copolymer flaked when scratched, and the 20/80 copolymer gave a checked surface on drying. The 30/70 copolymer produced a tough, coherent film, whereas the 40/60 and 50/50 copolymers were definitely rubbery.

PHYSICAL PROPERTIES OF BUTADIENE-STYRENE COPOLYMERS

Table IV summarizes the various properties determined on the six solid experimental polymers. The butadiene content, as obtained by iodine number determination, was within 1 to 3 per cent of the charging ratio employed. Physical properties of the raw polymers were determined by American Society for Testing Materials specifications wherever applicable. Samples for testing purposes were molded as follows.

Following a 3-minute warm-up period, the samples were molded for 10 minutes and the molds were cooled before removal of samples. The first three were molded at 290° F, the last three at 250° F.

TABLE IV
PHYSICAL CHARACTERISTICS OF BUTADIENE-STYRENE COPOLYMERS

	1	2	3	4	5	6
B-S charge ratio	0/100	10/90	20/80	30/70	40/60	50/50
Butadiene content (from iodine number)	0	10.8	19.2	28.8	37.6	47.3
Tensile strength (lb./sq. in.)	—	3750 ^a	2300 ^a	800 ^b	200 ^b	100 ^b
Ultimate elongation (%)	1.25 ^a	1.5 ^a	270 ^a	400 ^b	440 ^b	500 ^b
Hardness						
Shore A ^c	98+	98+	98+	84	35	27
Shore D	81	80	68	38	16	12
Water absorption (%)	0.10	0.10	0.10	0.10	0.10	0.10
Olsen stiffness (inch-lb. ^d)	10.56 ^f	12.00 ^g	3.2	0.25	0.07	0.05
Refractive index, (25° C ^h)	1.5935	1.5893	1.5858	1.5769	1.5682	1.5592
Specific gravity, (25° C ^h)	1.0530	1.0467	1.0335	1.0179	0.9976	0.9795
Izod impact, notched, (inch-lb. ⁱ)	2	2	2	—	—	—
Heat distortion point, (° F ^j)	142	106	66	33	21	5

^a Determined on horizontal Scott tester; this machine not suitable for polystyrene.

^b Determined on Goodyear autographic tensile elongation testing machine.

^c A.S.T.M. D 676-47T.

^d A.S.T.M. D 570-42.

^e A.S.T.M. D 747-48T.

^f Sample brittle, broke at 27°.

^g Sample stiff, reached max. load at 24°.

^h Determined on Abbé refractometer by grazing technique.

ⁱ A.S.T.M. D 792-48.

^j A.S.T.M. D 256-47T.

^k A.S.T.M. D 648-48Ta.

As the butadiene content increased, the maximum tensile strength dropped rapidly from 3750 to 100 pounds per square inch, whereas the ultimate elongation increased from 1.5 to 500 per cent. The tensile strength and elongation values are plotted as a function of butadiene content in Figure 2. The Shore hardness exhibited a marked drop with increasing butadiene content, the D values ranging from 80 to 12.

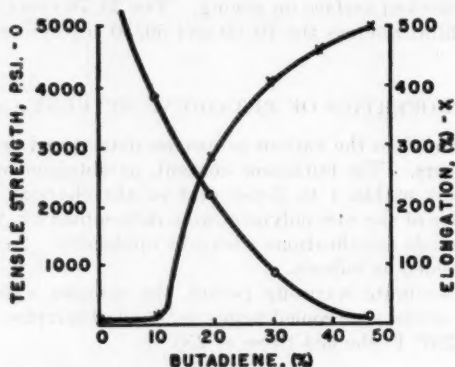


FIG. 2.—Tensile strength and elongation vs. butadiene content.

Water absorption values were low and independent of the copolymer composition.

Olsen stiffness values varied tremendously with increasing butadiene content, as would be expected in view of the change from the hard plastic stage to a soft, rubbery stage.

Refractive index and specific gravity values decreased in a fairly regular fashion with increasing butadiene content, as one could predict from the polymer composition. However, as plotted in Figures 3 and 4, the variation in these values is not a strictly linear function of the butadiene content.

Notched Izod impact values of 2 inch-pounds were obtained on the first three polymers. The last three polymers were not sufficiently rigid for this determination.

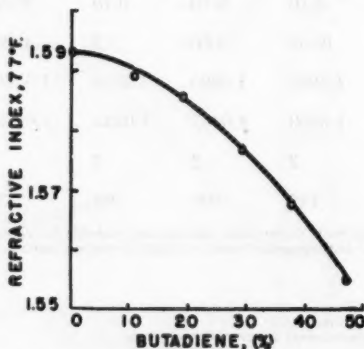


FIG. 3.—Refractive index vs. butadiene content.

The heat distortion points varied in a regular fashion from 142° to 5° F in a comparison of polystyrene with the copolymers of increasing butadiene content, and are plotted in Figure 5. The values obtained in this test depend on the stress imposed on the sample; considerably higher values can be obtained at lower stress.

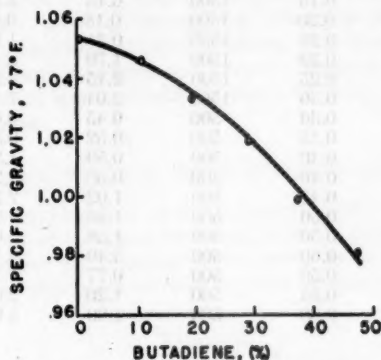


Fig. 4.—Specific gravity as function of butadiene content.

Data obtained with the Olsen flow tester illustrate the effect of temperature and pressure on these polymers (Table V). For a given polymer it is readily seen that with increase in temperature from 212° to 270° F, a large increase in rate of extrusion occurs at a fixed pressure. As the butadiene content of the polymer increases, a large increase in rate of extrusion occurs; the change ap-

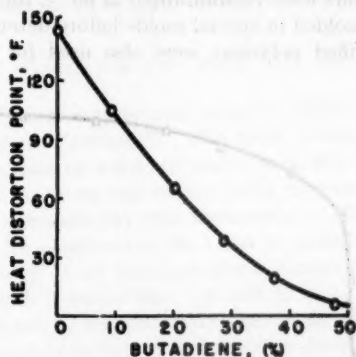


Fig. 5.—Heat distortion point vs. butadiene content.
(A.S.T.M. D 648A)

peared to be directly related to the polymer composition up to 40 per cent butadiene. The modifier content also had a significant effect on the extrusion rates. Presumably the lower rates obtained with the 50/50 copolymer were due to the rubberlike rather than plastic nature of the material.

Compression deflections are plotted in Figure 6 for polystyrene and the 10/90 and 20/80 butadiene-styrene copolymers. The first two exhibited

TABLE V

OLSEN FLOW CHARACTERISTICS OF BUTADIENE-STYRENE COPOLYMERS

Sample no.	Butadiene (%)	Dodecanethiol	Olsen flow (inches per minute)			
			Lb./sq. in.	212° F	240° F	270° F
7	0	0.15	1500	0.15	0.74	3.7
8	0	0.20	1500	0.18	0.90	4.3
9	0	0.25	1500	0.21	1.10	5.15
10	10	0.20	1500	1.70	6.45	22.5
11	10	0.25	1500	2.15	8.7	33.0
12	10	0.30	1500	2.04	7.4	33.0
13	20	0.30	500	0.45	0.68	1.6
14	20	0.35	500	0.52	0.87	2.35
15	20	0.40	500	0.59	1.26	3.65
16	30	0.40	500	0.66	1.28	2.7
17	30	0.45	500	1.02	2.27	5.35
18	20	0.50	500	1.45	3.23	6.45
19	40	0.50	500	1.38	2.65	5.2
20	40	0.60	500	3.40	6.4	12.0
21	50	0.50	500	0.77	1.30	2.62
22	50	0.55	500	1.20	2.0	3.9
23	50	0.60	500	1.80	3.0	6.0

practically identical behavior, shattering before any appreciable deflection occurred. The 20/80 copolymer, however, behaved entirely differently, producing a well defined yield point. The polymers containing larger amounts of butadiene were not suitable for this test.

Electrical properties, as listed in Table VI, were determined on samples prepared by coagulating a portion of antioxidant-free latex with 2-propanol and washing the precipitated polymer three times with fresh alcohol for 5 minutes. The polymers were vacuum-dried at 60° C for 20 hours. The dried polymers were then molded in special molds before determination of electrical properties. The purified polymers were also used for determination of re-

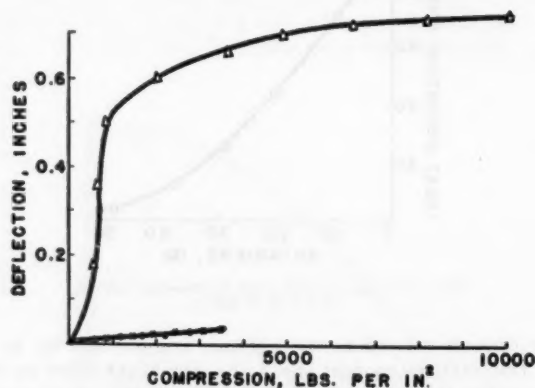


FIG. 6.—Compression-deflection as function of butadiene content.

X. B-S 0/100
O. B-S 10/90
Δ. B-S 20/80

fractive index. For comparison, samples of polystyrene were prepared by ordinary coagulation and by the procedure just described. The latter sample exhibited significantly lower power and loss factors. With increasing butadiene content, no significant change occurred in the dielectric constant, but the power factor and loss factor increased appreciably.

Oxygen absorption measurements were also carried out on the raw polymers at 150° C. It was found that, whereas polystyrene absorbed no appreciable oxygen in 100 hours, polymers containing butadiene absorbed appreciable amounts of oxygen proportional to the butadiene content of the polymer. The data are only of qualitative significance, however, because under the conditions these uncured polymers tended to shrink unevenly, thus changing the amount of exposed surface area.

APPLICATIONS OF HIGH-STYRENE RESINS

No compounding evaluation of the polymers prepared for this study was carried out. In view of the great importance which high-styrene resins have achieved in the past few years in the rubber and plastics industry, however, it seems appropriate at this point to refer to the voluminous technical literature

TABLE VI
ELECTRICAL CHARACTERISTICS OF BUTADIENE-STYRENE COPOLYMERS^a

	1	1U	2	3	4	5 ^b	6 ^b
B-S charge ratio	0/100	0/100	10/90	20/80	30/70	40/60	50/50
Dielectric constant	2.74	2.73	2.80	2.70	2.73	—	—
Power factor	0.0163	0.0235	0.025	0.146	0.79	—	—
Loss factor	0.00045	0.00064	0.0007	0.004	0.02	—	—

^a All polymers extracted with 2-propanol except 1U. Tests made on dry samples at 35° C and 1 kc. frequency.

^b Satisfactory test samples could not be molded from raw polymers.

on the applications which have been made with the commercially available resins.

The use of the various commercial resins in rubber compounding has been described by a number of authors²⁰. The usual procedure in mixing the compound is to band the resin on a hot mill and then slowly add the rubber. Either natural rubber or a wide variety of synthetic polymers exhibits varying degrees of mechanical compatibility with these resins. The rest of the compounding ingredients (sulfur, accelerator, etc.) can be added subsequently on a cool mill. Banbury mixing of all the ingredients except sulfur is readily accomplished, and the sulfur is added later by mill mixing. Recently, considerable interest has been shown in so-called easy processing resins²¹.

High-styrene resins have been shown to be of particular benefit when compounded with synthetic rubbers, although valuable results can also be obtained with natural rubber. In general, the effects of adding increasing amounts of the resins to GR-S, for example, are to increase the tensile strength, percentage elongation, tear resistance, hardness, stiffness, and flex life. Other advantages noted are improved processing, primarily due to less nerve in the stock, and improved electrical properties of the finished article. Calender shrinkage is also greatly reduced.

The properties of natural rubber vulcanizates containing high-styrene resins are different in some respects from those obtained with GR-S or nitrile rubbers. The stiffness, hardness, and abrasion resistance are increased, but the tensile strength, percentage elongation, tear resistance, and flex life tend to decrease, although the deterioration is not severe with 10 to 20 parts of resin per 100 parts of rubber. These differences are not unexpected, if one recalls that the gum stock properties of natural rubber are excellent, whereas those of the synthetic rubbers mentioned are relatively poor. The properties imparted to rubber stocks by the addition of these resins have been well summarized by Aiken²².

In the rubber reinforcing field, these resins have found particular application in the manufacture of shoe soles and heels, rubber flooring, hard board stocks, gaskets, caster wheels, electrical insulation, hard rubber stocks, and many other mechanical goods. Hoover²³ recently stated that 35 per cent of "leather" shoe soles made in 1949 probably consisted of combinations of synthetic rubber and special butadiene-styrene resins.

In the impact-resistant plastics field, where a relatively small amount of rubber is used to plasticize the resin, many interesting applications²⁴ have been made, such as golf ball covers, cutting blocks or beam punch pads, football helmets, bowling balls, luggage, printing plates, and golf club heads.

High-styrene resins have also found considerable utility in protective coatings and other solution applications. The use of such a resin (Pliolite S-5) in concrete floor finishes, stucco paints, traffic paints, and plaster sealers has been reported by several investigators²⁵. Coatings based on this resin are characterized by alkali resistance, waterproofness, abrasion resistance, and good adhesion.

Another recent solution application of considerable interest is in the formulation of heat-sealing, creaseproof, water vaporproof coatings for paper. For this use another high-styrene resin, Pliolite S-7, has appeared on the market in solution form or in compounded forms.

Because the high-styrene resins are usually prepared by emulsion polymerization methods, the unique opportunity exists of applying them to latex compounding. Little has been published in this field, but large scale applications are rapidly being developed.

Irvin²⁶ described the water dispersion (Marmix) of a high-styrene resin and its application to latex compounding with GR-S and butadiene-acrylonitrile copolymer latexes. Weatherford and Knapp²⁷ discussed the properties and applications of a latex (Pliolite Latex 190) containing a resinous copolymer of about 10 per cent butadiene and 90 per cent styrene. Applications mentioned are molded toys and sport equipment, dipped goods, latex threads, paper impregnants, fabric coatings, latex foams, and wire and cable insulation. Storey and Williams²⁸ studied latex blends of styrene resins and GR-S.

Finally, the use of high-styrene latexes in emulsion paints is rapidly assuming prominence. Ludwig¹⁹ and Ryden, Britt, and Visger³⁰ recently described the use of Dow Latex 512-K (containing a 40/60 butadiene-styrene copolymer), with and without the use of high-styrene resin latex, in this application. Ryden³¹ claimed a paint comprising a butadiene-styrene copolymer latex of a certain composition, plus pigments and other suitable compounding ingredients. Emulsion paints based on Chemigum Latex 101 (containing a 45/55 butadiene-styrene copolymer) were also described recently by Burr and Matvey³². Emulsion paints exhibit a number of advantages over conventional oil paints, such as

freedom from paint odor, excellent washability, and inertness to alkaline materials. McIntyre and co-workers¹³ discussed styrene-butadiene copolymer latices as raw materials for the coatings industry.

During the past five years, the use of high-styrene resins has shown a continuous growth because of their enthusiastic reception in the rubber, plastics, paint, and other fields. It is conservatively estimated¹⁴ that 25,000,000 pounds of these resins were manufactured in 1949. As new and better polymers specifically tailored for specific applications become available, it is certain that the total production of butadiene-styrene resinous copolymers will show a substantial increase in the near future.

SUMMARY

Although high-styrene resins have become of great commercial importance during the past 5 years (approximately 25,000,000 pounds manufactured in 1949), comparatively little information on the polymerization processes or any systematic review of their properties can be found in the technical literature. The object of the present paper is to supply such information.

A series of butadiene-styrene copolymers with charging ratios of 50/50, 40/60, 30/70, 20/80, and 10/90 was prepared. Polystyrene, prepared under the same conditions, was included as a control. Properties of the latexes and resins obtained, presented in a systematic manner, were found to be largely dependent on the monomer ratio employed in the polymerization.

For the first time a coherent picture is presented of the entire plastic range of the styrene-butadiene resins. This should encourage the further development of this large and expanding field, which includes such applications as natural and synthetic rubber reinforcing, impact resistant compositions, protective coatings, and latex paints.

ACKNOWLEDGMENT

The authors are grateful to W. T. Van Orman and the Rubber and Plastics Testing Department for obtaining molding and test data, to S. D. Gehman and R. B. Stambaugh of the Physical Research Division for electrical data, and to the Goodyear Tire and Rubber Co., for permission to publish this paper.

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POLYSULFIDE POLYMERS *

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Since the commercial introduction in 1929 of polysulfide polymers, they have been utilized for many types of applications in many industries. Their use is not large in volume compared with general purpose synthetic rubbers, but their excellent oil and solvent resistance as well as good aging properties make them valuable for special applications.

The purpose of this article is to describe all of the crude rubbers, latexes, and liquid polymers now manufactured¹. The variations that can be introduced to provide new materials with almost any desired characteristics will also be stressed.

POLYMER PREPARATION

The preparation of polysulfide polymers² is an example of condensation polymerization which consists simply of the reaction of an alkaline polysulfide with a suitable dihalide, as illustrated by the reaction of ethylene dichloride with aqueous sodium tetrasulfide:



By using a dispersing agent such as magnesium hydroxide, the polymer is obtained in the form of a suspension of particles 3 to 15 microns in size. Because of this particle size and the high specific gravity of the polymer, the dispersion settles readily, and can be washed free of electrolytes by successive decantations.

INORGANIC POLYSULFIDES *

There are several methods of preparing solutions of sodium polysulfide of varying ranks.

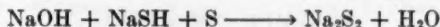
1. Reaction of sodium hydroxide with sulfur:



2. Reaction of sodium sulfide with sulfur:



3. Reaction of sodium hydroxide, sodium hydrosulfide, and sulfur:



4. Reaction of sodium with sulfur:



Rank is defined as the number of sulfur atoms present in the anion; thus sodium disulfide has a rank of 2.0, calcium tetrasulfide a rank of 4.0. A sodium poly-

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 42, No. 11, pages 2217-2223, November 1950.

sulfide of rank 1.5 represents an equimolar mixture of sodium monosulfide and sodium disulfide.

The reaction of sodium hydroxide with sulfur is at present the most economical method for producing sodium polysulfide solutions of rank 2.00 to 4.50. The sodium thiosulfate produced by the reaction does not influence the polymerization reaction. It is known that aliphatic halides react with sodium thiosulfate to form sodium alkyl thiosulfates. These salts can be converted to disulfides by oxidizing agents, such as iodine and hydrogen peroxide³. If these types of compounds are formed in the reaction, they must be converted to disulfides by the alkaline sodium polysulfide solution present.

Methods 2 and 3 are useful in preparing sodium polysulfide solutions of ranks between 1.00 and 2.00, which are difficult to prepare from sodium hydroxide and sulfur without relatively long reaction times or without use of temperatures above the boiling point of the solution.

Method 4 is useful in preparing pure sodium polysulfides for research investigations. The reaction can be conducted in a solvent such as alcohol or in liquid ammonia⁴.

DIHALIDES

A large number of organic dihalides can be used in the preparation of polysulfide polymers, although the number of halides commercially available is very small. The suitable halides which are industrially available are methylene dichloride, ethylene dichloride, propylene dichloride, glycerol dichlorohydrin, dichloroethyl ether, dichloroethyl formal, and triglycol dichloride. Satisfactory polymers and copolymers can be prepared from all of these raw materials. Polymers have been prepared also from dichloroethyl sulfide⁵. This material, although not generally available, has been produced in large quantities.

A great many dihalides have been used in laboratory investigations with varying success. Some generalizations can be made:

1. The bromides are more reactive than the chlorides, and yield the same polymeric products, inasmuch as the halogen is eliminated as sodium chloride or bromide.
2. The halogen has to be aliphatic in character for easy reactivity. Chlorine atoms attached to double-bonded carbon atoms and attached to aromatic rings are relatively unreactive. Under severe reaction conditions⁶ and when activated, as by a nitro group⁷, aromatic chlorides are reactive with sodium polysulfide.
3. Primary chlorines are more reactive than secondary which are in turn more reactive than tertiary.

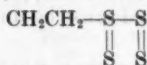
A systematic survey of the physical properties of polymers from different dihalides is being made at present in the authors' laboratory and will be reported on in the future.

POLYMER STRUCTURE

The structure of the organic disulfide polymers is represented unequivocally by a repeating segment $(R-SS)_n$. The polymers are polymeric disulfides and are capable of undergoing the normal reactions common to simple organic disulfides. Vigorous reduction of polyethylene disulfide yields ethanedithiol, and oxidation of ethanedithiol produces a polymer closely resembling the original polymer⁸. Oxidation with nitric acid produces ethanedisulfonic acid⁹.

The original proposal of Patrick¹⁰ for a structure of the polysulfide tetra-

sulfides having two sulfur atoms in the linear chain and two coordinate sulfur atoms on the side of the chain:



was based on the easy removal of two of the sulfurs by treatment of a water dispersion of polymer with sodium hydroxide, sulfide, or sulfite and also by the x-ray diffraction data of Katz¹¹. There have been many investigations on the structure of polysulfides since that time. Physical methods such as molecular refraction¹² viscosity¹³, parachor¹⁴, x-ray diffraction¹⁵, electron diffraction¹⁶, and ultraviolet spectra¹⁷, have been widely used, as well as the use of chemical evidence¹⁸. While the question of the exact structure cannot be regarded as settled, there is a preponderance of evidence for the linear trisulfide configuration, at least in the trisulfides. The tetrasulfide structure is less certain. In the above references, the tetrasulfides have been postulated, depending on the authors, to contain, one, two, three, or four sulfur atoms in the linear chain, with the remainder, if any, coordinated on the side.

The end groups of the high molecular weight polymers produced by the normal reaction are not definitely known. As an excess of sodium polysulfide is customarily used in the polymerization, it is doubtful that chlorine terminals would be present. Thiol terminals have been postulated¹⁹; however, extensive experimental work carried out in recent years with polymers known to contain thiol terminals makes that postulate probably incorrect. Slight hydrolysis of the aliphatic dihalides by the high alkalinity of the sodium polysulfide solution to produce hydroxyl terminals now appears to be the most reasonable assumption.

In spite of the relatively few commercial dihalides available, a large number of different products can be produced. Variations in the ratio of dihalides, in the amount of cross-linking agent, in the sulfur rank, in the type of chain terminal, and in the molecular weight, can be employed to produce polymers with desired characteristics.

Copolymers from ethylene dichloride and dichloroethyl formal have properties intermediate between the two polymers. Polyethylene disulfide is a hard rigid plastic having elastomer characteristics only above 212° F. The formal disulfide is a rubber down to -65° F. The transition point and other physical properties of the copolymers depend chiefly on the ratio of the two dihalides.

Trifunctional halides, such as trichloropropane, and even tetrafunctional halides can be used to produce branched or cross-linked structures. This method is necessary to obtain such a structure, as the vulcanization techniques now used do not cause cross-linking of chains. Use of a cross-linked polymer is necessary to obtain the best compression set resistance.

The polysulfide polymers can be partially reduced to cleave disulfide groups and form thiol terminals¹⁹. The molecular weight of the final product can be controlled so that polymers ranging from fluid liquids to millable crude rubbers can be readily obtained. Oxidation of the low polymers to reform disulfide groups regenerates the original high molecular-weight elastomer.

Other terminals can be substituted for thiol by using monofunctional halides. Butyl chloride can be used to obtain an unoxidizable polymer, with a butyl group on each end of the chain. Ethylene chlorohydrin can be used to produce hydroxyl groups, and chloroacetic acid can be used to produce carboxyl ter-

minals. The molecular weight of the final polymer is governed by the ratio of monohalide to dihalide used. This technique has the one limitation that the other functional group introduced must be unreactive toward sodium polysulfide solutions.

COMMERCIAL POLYMERS

The polysulfide polymers are supplied as crude rubbers, water dispersions, and liquid polymers.

Table I shows the structures of the available crude rubbers. These materials are processable on conventional rubber equipment. Unlike natural rubber, polysulfide elastomers do not undergo breakdown to a workable plasticity on the rubber mill. It is necessary to plasticize chemically Thiokol Type A and Type FA by using materials such as benzothiazolyl disulfide or tetramethylthiuram disulfide. These chemicals reduce the plasticity of the polymer by causing scission of disulfide linkages and thus reducing molecular weight. This effect is only temporary, as these linkages are reformed in the vulcanization. Polymers which contain thiol terminals, Type ST and PR-1, have their molecular weight adjusted so they are in the millable crude range without further chemical plasticization.

TABLE I
POLYSULFIDE CRUDE RUBBERS

Thiokol	Halide	Rank	Cross-linked	Terminals
Type A	Ethylene dichloride	4.0	No	Unknown
Type FA	Ethylene dichloride Dichloroethyl formal	1.8	No	Unknown
Type ST	Dichloroethyl formal	2.25	Yes	Thiol
PR-1	Ethylene dichloride Dichloroethyl formal	2.0	Yes	Thiol

The liquid polymers are fairly low molecular-weight polymers, and are prepared from dichloroethyl formal with a small amount of trifunctional halide. Table II shows the properties of the two commercial liquid polymers (LP-2 and LP-3) and the one pilot plant polymer available.

The solvents listed as limited are compatible with the liquid polymers up to a definite amount. Beyond this amount, two layers are formed. The compatible amount varies with the particular solvent and the molecular weight of the liquid polymer.

The properties of the four latexes manufactured are shown in Table III. Type MX differs from WD-6 only in containing less propylene dichloride.

TABLE II
POLYSULFIDE LIQUID POLYMERS

	LP-2	LP-3	ZL-100
Molecular weight (av.)	4000	1000	300
Viscosity (poises)	450	10	0.5
pH	6 to 8	5 to 6	5 to 6

Solvents: Benzene, toluene, dioxane, cyclohexanone, furfural, ethylene dichloride, phenol, dibutyl phthalate, tricresyl phosphate.

Limited solvents: Xylene, acetone, methylethyl ketone, ethyl acetate, butyl acetate, carbon tetrachloride, 2-nitropropane.

Nonsolvents: Aliphatic hydrocarbons, methanol, ethyl alcohol, butyl alcohol.

TABLE III
THIOL WATER DISPERSIONS

Polymer	Composition	Particle size (microns)	Odor	Solvent resistance	Water resistance
Type MX	Ethylene dichloride	2 to 6	Very poor	Wxeellent	Good
	Propylene dichloride				
WD-6	Ethylene dichloride	2 to 6	Very poor	Excellent	Good
	Propylene dichloride				
Type MF	Ethylene dichloride	4 to 8	Poor	Very good	Good
	Dichloroethyl formal				
WD-2	Dichloroethyl formal	8 to 15	Very slight	Good	Good
	Trichloropropane				

Propylene dichloride has a softening effect on the copolymer; WD-6 contains enough propylene dichloride to deposit a continuous film on drying. The latexes are all high molecular weight polymers without active terminals.

VULCANIZATION

CRUDE RUBBERS

The two distinct classes of crude rubber which have been manufactured are:

I. High molecular-weight polymers with unknown end groups which require chemical plasticization and which are vulcanized with zinc oxide.

II. Polymers with thiol end groups which require no chemical plasticization and which are vulcanized with oxidizing agents.

The type of terminal is the more basic factor in differentiating the two classes, as the polymers in class I can be preplasticized with the usual agents in the latex form to produce crude rubbers which require no mill plasticization. As zinc oxide is an oxidizing agent, it also can be used in vulcanizing polymers in class II.

Types A and FA are the two crude rubbers belonging in class I. Types B, D, and F, which are no longer manufactured, also belonged there²⁰. Plasticiza-

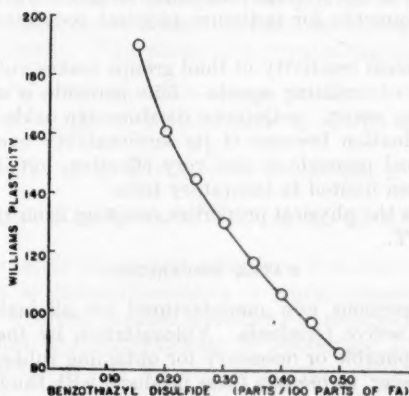


FIG. 1.—Effect of amount of benzothiazyl disulfide on Williams plasticity of Thiokol Type FA.

tion works by chain scission, so extremely small quantities of chemicals are needed and the amounts must be carefully controlled. Figure 1 shows the effect of benzothiazolyl disulfide on the plasticity of Thiokol Type FA. Many of the organic thiols and disulfides used as accelerators in the rubber industry can be used. Blacks are needed in compounding to achieve the best physical properties, although a number of other reinforcing pigments can be used. As noted, zinc oxide is usually used as the vulcanizing agent. The vulcanization probably consists of linking together the unknown end groups. The vulcanizates from these two polymers are poor in compression set resistance, so it seems improbable that a cross-linked structure is developed. The stress relaxation data to be discussed supports this concept, as does the fact that a minimum amount of zinc oxide is necessary for vulcanization. Additional amounts have little effect on the characteristics of the vulcanizate.

TABLE IV
TYPICAL FORMULATIONS OF THIOKOL TYPE ST

Thiokol Type ST	100	100	100
SRF black	60	60	60
Stearic acid	3	1	1
<i>p</i> -Quinone dioxime ^a	1.5	—	—
Zinc oxide	0.5	—	—
Zinc peroxide	—	4.0	—
Lead peroxide	—	—	3.0
Tensile ^b	1250	1250	1275
Elongation	310	300	220
Hardness ^c	69	70	73
Compression set ^d	35	100	55

^a GMF sold by Naugatuck Chemical Co.

^b Cure, 30 min. at 287° F.

^c Shore Durometer A.

^d A.S.T.M. Method B, 22 hr. at 158° F.

Type ST and PR-1 belong in class II. The molecular weights are adjusted to make the polymers suitable for most processes without any plasticization. When further plasticization is required, the liquid polymers LP-2 or LP-3 can be utilized to reduce the average molecular weight. Carbon blacks are the best reinforcing pigments for optimum physical properties, although others can be used.

The great chemical reactivity of thiol groups makes vulcanization possible by a wide variety of oxidizing agents. Zinc peroxide is an effective nondiscoloring vulcanizing agent. *p*-Quinone dioxime-zinc oxide is the most widely used curing combination because of its serviceability over a wide range of temperatures. Lead peroxide is also very effective, but it is too difficult to control and has been limited to laboratory tests.

Table IV shows the physical properties resulting from typical formulations of Thiokol Type ST.

WATER DISPERSIONS

The water dispersions now manufactured are all high molecular-weight polymers without active terminals. Vulcanization by the two methods described are not applicable or necessary for obtaining rubbery films on drying. It is possible, however, to prepare these products with thiol terminals. When used alone, these latexes (except for WD-6) require chemical softening with am-

monium hydrosulfide or tetramethylthiuram disulfide. These chemicals produce a transient softening, so a continuous latex film is deposited. The effect disappears as the latex film ages at room temperature; the rate depends on the softener used.

LIQUID POLYMERS

These materials have thiol end groups, and can be converted to rubbers by oxidizing agents, even at room temperatures. Any reagent which is capable of reacting with two thiol groups can be potentially useful as a curing agent. Diisocyanates, for example, can be used not only with the thiol-terminated liquid polymers, but also with the experimental hydroxyl-terminated polymers. Furfural with an acidic catalyst also acts as a vulcanizing agent.

The highest molecular weight product, LP-2, is usable in most applications. It can be compounded by adding reinforcing fillers and pigments on a 3-roll paint mill, colloid mill, ball mill, or internal mixer. Table V shows some of the curing agents that can be used.

TABLE V
VULCANIZATION OF THIOKOL LP-2

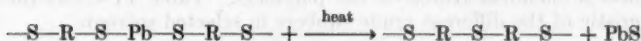
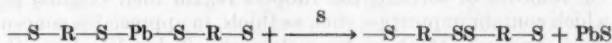
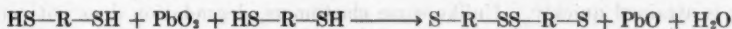
Oxidizing agent	Catalyst	Range		Maximum service temp. (° F)
		Temp. (° F)	Time	
Lead peroxide	—	0-200	5 min. to 48 hr.	350
Cumene hydroperoxide	DPG ^a	0-100	10 min. to 8 hr.	160
Zinc oxide	Hexa ^b	50-250	8 hr. to 48 hr.	160
<i>p</i> -Quinone dioxime ^c	DPG	70-250	8 hr. to 48 hr.	350
Zinc peroxide	Ammonia	70-150	1 day to 2 days	350
Cobalt salts	—	70-150	4 hr. to 1 day	350
Furfural	Formic acid	70-100	1 day to 3 days	160

^a Diphenylguanidine.

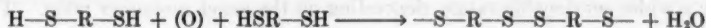
^b Hexamethylenetetramine.

^c GMF, Naugatuck Chemical Co.

Lead peroxide is one of the most versatile curing agents; it will bring about vulcanization at room or elevated temperatures. It can be retarded with stearic or oleic acids to obtain an 8-hour pot life after addition of the lead peroxide. The lead peroxide can be added as a dry powder on the paint mill, or a previously prepared dispersion in solvent or plasticizer can be simply stirred into the liquid polymer directly. The mechanism of vulcanization is believed to be:



Cumene hydroperoxide is a soluble curative. It is only moderately active, and activators such as diphenylguanidine or triphenylguanidine are customarily used with it. Whereas organic peroxides are generally used as catalysts in polymeric systems, the requirements in converting LP-2 are based on stoichiometric quantities as only the available oxygen enters into the reaction.



The medium molecular weight product, LP-3, is used as an impregnant or where very fluid formulations are required. As a larger amount of vulcanizing agent is needed, the cure is more difficult to control, owing to the exothermic character of the oxidation reaction. The *p*-quinone dioxime-diphenylguanidine combination or a cobalt drier usually are used. The mechanism of the latter cure is similar to the action of cobalt in catalyzing the conversion of drying oils. Since oxygen in the air is required, the conversion is possible only in thin films.

ZL-100 is used mainly as a chemical modifier in phenolic-type resins. It is too reactive to metallic oxidizing agents or organic peroxides, although the product has been converted to a high polymer with cobalt driers.

PROPERTIES

Regardless of the initial physical state of the polymers, crude rubber, latex, or liquid polymers, the properties of the high molecular weight materials depend mainly on their chemical structure. Polysulfide polymers are outstanding for solvent and oil resistance²¹, impermeability to vapors and gases²², and resistance to oxygen, light, and ozone²³. They do not have high tensile strength or abrasion resistance, but are suitable, in general, for mechanical rubber goods.

TABLE VI

VOLUME SWELL OF COMMERCIAL POLYSULFIDE POLYMERS IN VARIOUS SOLVENTS^a

Polymer	Sulfur (%)	SR-10 ^b	SR-6 ^c	Benzene	Methyl-ethyl ketone	Carbon tetrachloride
Type A	85	0	5	18	12	7
PR-1	55	2	10	68	23	29
Type FA	47	3	13	100	33	40
Type ST	40	5	15	127	49	48

^a Per cent volume increase after 1-month immersion at 80° F.

^b A.S.T.M. D 471-46T standard reference fuel No. 1 (diisobutylene).

^c A.S.T.M. D 471-46T standard reference fuel No. 2 (60% diisobutylene, 40% aromatics).

Disadvantages often cited against them have been odor and poor compression set resistance.

SOLVENT RESISTANCE

The resistance to swelling by solvents depends largely on the weight-per cent of sulfur in the polymer structure. On exposure to solvent, equilibrium swelling is attained quickly. Unlike some elastomers, degradation does not occur as a result of solvent action because of the resistance of polysulfide to oxidative attack. On removal of solvent, the rubbers regain their original properties. Solvents which contain impurities, such as thiols, in appreciable concentrations, do promote a chemical attack on the polymers. Table VI shows the results characteristic of the different crude rubbers in selected solvents.

TEMPERATURE RANGE

The polymers which are prepared mainly from ethylene dichloride (Type A, Type MX, and WD-6) become hard at temperatures of about -20° F and become fairly soft at temperatures in the vicinity of 180° F. Copolymers from ethylene dichloride and dichloroethyl formal (Type MF, Type FA, and PR-1) have a wider serviceable range, depending on the exact monomer ratio. They

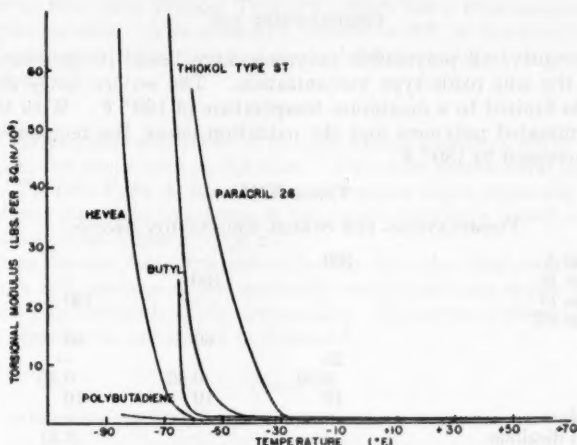


Fig. 2.—Effect of temperature on torsional modulus of elastomers.

are satisfactory in a temperature range of about -35° to 300° F. The polymers based on dichloroethyl formal alone have an extremely wide range in which they maintain the properties of an elastomer. Depending on the specific application, they can be used from -65° to 350° F. Figure 2 shows the change or torsional modulus²⁴ with temperature of Thiokol Type ST and several other elastomers. Formulations used are given in Table VII. Data on some of the other polysulfide polymers have been published using different methods of testing.²⁵

TABLE VII
FORMULATIONS OF RUBBERS FOR TORSIONAL TEST

Polybutadiene	100	—	—	—	—
Butyl	—	100	—	—	—
Hevea	—	—	100	—	—
Paracril-26	—	—	—	100	—
Thiokol Type ST	—	—	—	—	100
EPC black	50	—	—	—	—
MPC black	—	25	—	—	—
MT black	—	—	80	—	—
SRF black	—	25	—	75	60
Stearic acid	1.5	1.0	1.0	1.0	1.0
Sulfur	2.0	2.0	2.0	1.5	—
Zinc oxide	5	5	5	5	—
Pine tar	—	—	5	—	—
Bardol	5	—	—	—	—
Petrolatum	—	2	—	—	—
TP-95	—	—	—	10	—
Tetramethylthiuram disulfide	—	1.0	—	—	—
Mercaptobenzothiazole	—	0.5	—	—	—
Benzothiazyl disulfide	3.0	—	1.0	2.5	—
Tellurac	—	0.5	—	—	—
Lead peroxide	—	—	—	—	3.0
Diphenylguanidine	—	—	0.2	—	—

COMPRESSION SET

Until recently, all polysulfide polymers were linear in structure and depended on the zinc oxide-type vulcanization. The service range under compression was limited to a maximum temperature of 100° F. With the advent of thiol-terminated polymers and the oxidation cures, the temperature range has been increased to 180° F.

TABLE VIII
FORMULATIONS FOR STRESS RELAXATION STOCKS

Thiokol Type A	100	—	—	—
Thiokol Type B	—	100	—	—
Thiokol Type D	—	—	100	—
Thiokol Type ST	—	—	—	100
SRF black	—	60	60	60
MPC black	25	—	—	—
Stearic acid	0.50	0.50	0.50	0.50
Zinc oxide	10	10	10	—
Lead peroxide	—	—	—	1.50
Benzothiazyl disulfide	—	—	0.30	—
Diphenylguanidine	—	—	0.10	—
Tetramethylthiuram disulfide	0.25	0.25	—	—
Cure (min./° F)	50/287	30/287	50/298	30/287
Tensile	790	820	1185	1160
Modulus, 100%	395	585	515	540
Modulus, 300%	745	1185	1185	—
Elongation, %	250	320	300	190
Hardness (Shore)	73	77	76	73

Using a stress relaxation balance²⁶, Tobolsky, Stern, and Mochulsky have examined this characteristic of the polysulfide polymers. In one article²⁷, they gave data for the stress relaxation of some of the various commercial polymers which were not identified as such. Table VIII shows the formulations with identification of polymers and Figure 3 shows their results on the relative diminution of stress of a sample held at a fixed elongation (50 per cent) as a function of time. Noting that the logarithm of time is plotted, one sees that there are very great differences in the behavior of the different polymers. The polymers that utilize the zinc oxide cure (type A, B, and D) are much more

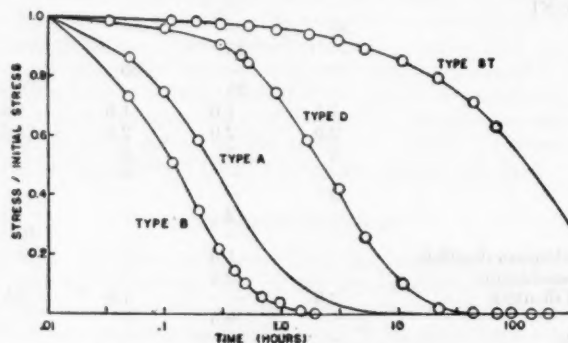


FIG. 3.—Stress relaxation of Thiokol polymers.

susceptible to flow than Thiokol Type ST, which has a thiol oxidation mechanism of vulcanization. The cross-link present in ST, or the substitution of a formal in place of an ether, does not account for the order of magnitude difference in behavior²⁸.

ODOR

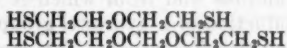
One of the physical properties of the polysulfide polymers which has been a disadvantage for many uses is the odor. The older commercial polymers, in particular, Thiokol Type A, have quite unpleasant odors especially when hot. This deficiency has been overcome in the newer polymers based on dichloroethyl formal such as Thiokol Type ST.

The three known factors which influence the odor characteristics of the polymers are the presence of low molecular-weight dithiols, stable cyclic compounds, and polymerizable cyclic compounds. Examples of these three classes of organic compounds are shown in Table IX.

TABLE IX

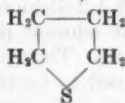
TYPES OF COMPOUNDS RESPONSIBLE FOR ODOR IN POLYSULFIDE POLYMERS

I. Low molecular-weight dithiols:

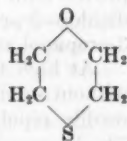


II. Stable cyclic compounds:

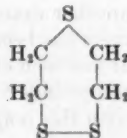
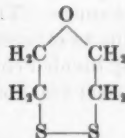
Thiacyclopentane



Thioxane



III. Polymerizable cyclic compounds:



Polymers which are processed so as to have thiol terminals can be controlled to a definite average molecular weight. There is always a distribution of molecular weight of individual polymer chains, so both higher and lower molecular weight species are present. Flory²⁹ has derived the equations giving the molecular-weight distribution as a function of extent of reaction for polyesters. These results would be equally applicable for polysulfide polymers which are produced by a condensation reaction. The amount of low molecular-weight dithiol present imparts an odor to the liquid polymers. The lower the average molecular weight, the greater is the amount of low molecular weight species and the stronger the odor. Polymers can be and have been prepared with corresponding molecular weights, but with hydroxyl instead of thiol terminals; these materials do not have a significant odor. As would be expected of thiol-terminated polymers, conversion by oxidation to high molecular-weight rubbers eliminates volatile dithiols and also the odor.

Stable rings are formed by the action of sodium monosulfide, always present in sodium polysulfides, with dihalides which are of suitable length to form five-

and six-membered monosulfide rings. 1,4-Dichlorobutane is converted almost completely to thiocyclopentane by reaction under normal conditions with sodium tetrasulfide. 1,4-Dichloro-2-butene, which has a double bond decreasing the flexibility of the four carbon chain, yields almost entirely linear polymer. Bis(2-chloroethyl) ether yields about half linear polymer and half monosulfide ring (thioxane). Thus the amount of stable ring is influenced by the length and structure of the dihalide³⁰. These stable ring compounds are odorous, but as they are immiscible with water, they can be removed fairly easily by steam distillation of the latex at the end of the polymerization step.

The polymerizable cyclic compounds are the materials believed responsible for the unpleasant odor of certain polysulfide polymers. Steam distillation of polysulfide water dispersions yields small amounts of polymerizable rings³¹. These rings repolymerize readily to yield high polymers³².

The ease of ring formation varies greatly with the length and type of the repeating unit in the polysulfide polymer chain³⁰. Polymers from methylene dichloride, ethylene dichloride, and 1,3-dichloropropane form ring compounds fairly readily. These three polymers are also among the most odorous. Dichloroethyl ether forms polymers which are much improved in odor and from which it is more difficult to obtain rings. Dichloroethyl formal forms polymers which are substantially odorless and from which it is extremely difficult to produce any rings. Introduction of a hydroxyl group into the polymer chain greatly diminishes odor and ring formation. This is shown in the greatly improved odor and diminished amount of cyclic compounds produced from 1,3-dichloro-2-propanol as contrasted with 1,3-dichloropropane, and 1,2-dichloro-3-propanol as contrasted with 1,2-dichloropropane³⁰.

At high temperatures, the odorous polysulfide polymers can be sublimed without significant degradation. The evolution of ring compounds which can readily repolymerize is believed to be the explanation for this phenomenon. The lacrymatory gases evolved on hot milling of Thiokol A are also probably another example of this mechanism. The odor of ethylene polysulfide polymers has been suggested as due to ethanedithiol³³, but this has been disputed⁹. It has been claimed that finely divided copper will remove the odor of ethylene tetrasulfide³⁴. Neither of the last two observations fit the authors' experiences with this polymer.

APPLICATIONS

CRUDE RUBBER

Practically all uses of polysulfide rubbers are due to the solvent and oil-resistant characteristics of the polymers. Underground concrete storage tanks lined with Thiokol sheeting have been in service for storing aviation fuel for six years. Major applications are printers' rolls and paint-spray hose. The combination of oil resistance and low temperature flexibility have proved of interest to the aircraft industry.

Several of the polysulfide polymers are readily adaptable to manufacture of putties and high-solids cements. The putties are nonhardening, adhere to a wide variety of surfaces (both porous and nonporous), and have remarkable aging qualities. These properties make them useful as sealants in the petroleum industry. A seal made with Thiokol putty is impermeable to water and oil. Putty in service below the normal water level in the tropics was found unchanged after six years' exposure.

LIQUID POLYMERS

The unusual properties of these products have resulted in a wide variety of applications. Compounds have found use as a leather impregnant, in the manufacture of oil seals, in the rubber industry as repair and coating material, in the aircraft industry as fuel tank and pressurized cabin sealants, in the electrical industry as seals and plotting compounds, in the marine industry as deck and hull caulking materials, and even in the mannikin and model industry as flexible rubber molds.

Some of these applications are due to the typical properties of the polysulfide elastomers, others are due to the liquid state of the products. Compounds can be prepared with fillers so that they are fluid compositions or thixotropic pastes. Solvents can be added in cases where a lower viscosity is needed and shrinkage can be tolerated. The specific formulation to be used depends on the application conditions. Compounds will withstand continuous temperatures of -65° to 300° F and even 350° F for intermittent service. All other properties, such as aging, ozone resistance, water and oil resistance, are in the range normally associated with Thiokol-type polymers.

Although solvents can be used with the liquid polymers because of their comparatively low molecular weight, the converted rubbers do not dissolve in these same solvents. Resistance to swelling is about the same as vulcanized Thiokol Type ST.

LATEXES

The latexes have properties similar to those of the crude rubbers and are used where it is desired to deposit an oil-resistant film. Some latex applications make use of high-solids aqueous putties, and have found general use in the aircraft industry in special sealants for integral fuel tanks.

The most important application for latex in the past has been for lining the walls of concrete storage tanks. This use has been developed further into coating steel tanks for the storage of sour crude.

It has been found possible to add Thiokol latexes to solutions of coating resins such as nitrocellulose, vinyl chloride copolymers, and vinylidene chloride copolymers to yield films suitable for protection of iron and steel structures. The water in the latex separates out resulting in slightly swollen polysulfide polymer particles suspended in a solvent solution of resin. The elastomer acts as a nonextractable plasticizer and also allows application of thicker films per coat. Films deposited from such mixtures have been found to have a high degree of impermeability to water.

There are other nonrubber uses in which polysulfide polymers have been utilized. The crude rubbers are useful for plasticizing sulfur cements²⁵. The liquid polymers are compatible with and react with resins made from phenol formaldehyde, furfuryl alcohol, and epichlorohydrin. The polysulfide chains act as nonextractable plasticizers for the hard brittle resin composition. A special polymer has been developed that can be flame-sprayed to produce a plastic coating on steel or other metals. This process has been in use by the Navy for years. With the improvements in the spray powder and in the methods of application perfected during this last year, this technique appears suitable for industrial applications.

SUMMARY

The chemistry of the condensation polymerization is reviewed briefly. The structures of the polymeric products as well as the effects of copolymeriza-

tion, cross-linking, end groups, and molecular weight upon polymer properties are discussed. The composition and properties of the commercial crude rubbers, water dispersions, and liquid polymers are presented together with ideas on the mechanism of their vulcanization. The reason for the odor of polysulfide polymers is discussed. Some information is presented on solvent resistance, stress relaxation, and other characteristics of the polymers. Applications for the different types of products are summarized.

ACKNOWLEDGMENTS

The authors are indebted to the laboratory staffs of the Development and Technical Service Departments, who have obtained much of the information upon which this article is based. The authors also wish to acknowledge the help of A. W. Meyer, W. A. Hermanot, and H. E. Haxo of the General Laboratories of the U. S. Rubber Company for developing the method and apparatus used in obtaining the data shown in Figure 2.

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POLYSULFIDE LIQUID POLYMERS *

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Polysulfide liquid polymers are a comparatively recent development conceived at the Thiokol Laboratories in 1943. The development was initiated by the problem of finding methods to reduce the molecular weight of a polysulfide rubber which was too tough to process on conventional rubber milling equipment. The problem was solved by reduction of a few of the disulfide links present in the polymer chain.

It was soon found that the method was applicable to the preparation of polymers low enough in molecular weight to be liquids. The method produces dithiols of high purity which are extremely active in a wide variety of chemical reactions. Some formulations have been developed which depend on conversion from the liquid to rubber state at temperatures as low as 50° F in about 30 minutes. Most of the converting agents function through oxidation with hydrogen removal from the thiol and a linkage of sulfurs to reform the disulfide group. The converted polymers have the general properties of polysulfide polymers: good solvent resistance to a wide range of solvents, low diffusion rate of gases, good resistance to oxidation, ozone, and weathering, and a service temperature range from -65° to +250° F. (Some compounds can withstand intermittent temperatures as high as +350° F.) The low temperature properties are inherent in the polymer and do not depend on special compounding techniques.

PREPARATION

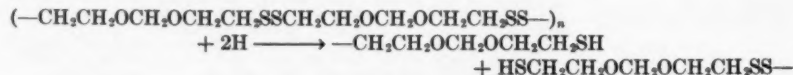
The preparation of polysulfide polymers by the reaction of organic dihalides and sodium polysulfide:



has been known for some time¹. If an excess of sodium polysulfide is used, rubbers of high molecular weight can be readily produced. It is possible to prepare liquids of low molecular weight in many cases by using a deficiency of sodium polysulfide. The products have chlorine terminals which are not easily coupled to form products of high molecular weight.

Thermal depolymerization has also been used to make liquid polymers², but this reaction is not readily reversed to reform the rubber.

The most practical method found has been reductive cleavage of disulfide groups to yield products which have thiol terminals.



The amount of depolymerization can be readily controlled and the liquid polymeric product can be reconverted to rubbers of high molecular weight by a

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 43, No. 2, pages 324-328, February 1951. This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its International Meeting in Cleveland, October 11-13, 1950.

wide variety of methods. As the disulfide group is usually present in polysulfide polymers, this type of depolymerization has a wide applicability.

Treatment of a water dispersion of a polysulfide polymer with sodium hydrosulfide and sodium sulfite³ is one method for controlled cleavage of high polymers. Depending on the mole ratio of sodium hydrosulfide to polymer repeating segments, liquid polymers of varying molecular weights can be readily prepared. The sodium hydrosulfide splits a disulfide link to form a thiol and a sodium salt of a thiol. The extra sulfur atom is taken up by the sodium sulfite:



The addition of acid to coagulate the liquid polymer water dispersion converts the sodium salt back to the free thiol.

While the commercial liquid polymers contain terminal thiol groups produced by the methods described, liquid polymers have been prepared experimentally with terminal alkyl, aryl, hydroxyl, allyl, and carboxyl groups. These materials can be produced by using a mixture of dihalide with the appropriate monohalide in the initial reaction with sodium polysulfide. The molecular weight of the product is easily controlled by the mole ratio of monohalide to dihalide.

The structure of the repeating chain segment can also be varied to produce liquid polymers of different chemical structures. While dichloroethyl formal is used in the commercial polymers, it is possible to use all the other dihalides adaptable to the reaction with sodium polysulfide. Ethylene dichloride, propylene dichloride, dichloroethyl ether, and triglycol dichloride ($ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$) can all be used alone or in mixtures to form copolymers. By using dihalides containing other functional groups, which must be unreactive with sodium polysulfide, polymers can be prepared containing that group distributed along the polymer chain. Thus use of glycerol dichlorohydrin, α,β -dichloropropionic acid, or dichloroethyl amine places hydroxyl, carboxyl, or secondary amino groups in the liquid polymer molecule.

PROPERTIES

The liquid polymers produced commercially are described in Table I.

These polymers are composed of 98 mole-per cent of dichloroethyl formal and 2 mole-per cent of trichloropropane. The vulcanized product thus consists of long linear chains held together by the small amount of trifunctionality placed in the polymer by the trichloropropane.

The polymers in the low molecular weight form are soluble in a wide variety of solvents. The lower the molecular weight, the higher the amount of solvent miscible with the polymer. Table II shows the amount of solvent which can be added to the liquid polymers, expressed as percentage by weight of solvent at the composition at which two phases begin to form.

TABLE I
COMMERCIAL LIQUID POLYMERS

	LP-2	LP-3	LP-4
Molecular weight (average)	4000	1000	300
Viscosity (poise)	450	10	0.5
pH	6 to 8	5 to 6	5 to 6
Specific gravity (20/20)	1.27	1.27	1.23

TABLE II
SOLUBILITY OF SOLVENTS IN THIOKOL LIQUID POLYMERS^a

	LP-2	LP-3	LP-8
Acids, organic			
Formic acid	20	20	M ^b
Acetic acid, glacial	0	0	0
Alcohols			
Methanol	0	0	25
Ethanol	0	0	20
1-Butanol	0	0	25
Ethylene glycol	0	0	0
Furfuryl alcohol	90	M	M
Glycerol	0	0	0
Aldehydes			
Benzaldehyde	M	M	M
Furfural	M	M	M
Ethers			
Diethyl ether	0	40	M
Dioxane	M	M	M
Ketones			
Acetone	50	80	M
Methyl ethyl ketone	70	M	M
Methyl isobutyl ketone	30	80	M
Cyclohexanone	M	M	M
Esters			
Methyl acetate	60	M	M
Ethyl acetate	50	M	M
Butyl acetate	50	M	M
Dibutyl phthalate	M	M	M
Tricresyl phosphate	M	M	M
Aromatic hydrocarbons			
Benzene	M	M	M
Toluene	M	M	M
Xylene	50	M	M
Chlorinated hydrocarbons			
Carbon tetrachloride	70	M	M
Ethylene dichloride	M	M	M
Ethylene chlorohydrin	90	M	M
Chlorobenzene	M	M	M
Nitroparaffins			
Nitromethane	60	M	M
Nitroethane	90	M	M
1-Nitropropane	90	M	M
2-Nitropropane	80	M	M

^a % by weight of solvent in liquid polymer.

^b M signifies miscible in all proportions.

There are no known solvents for the converted polymers of high molecular weight. They swell in solvents, but cannot be put into solution without molecular weight reduction. Solutions can be made by addition of small amounts of agents such as thiols, which reduce disulfide groups, or strong acids which can sever formal linkages.

In a neutral pH, organic thiols are very resistant to conversion to disulfides by atmospheric oxygen. These polymeric thiols are, therefore, stable at room temperatures. High temperatures or an alkaline environment cause a change in viscosity with time.

For a specific polymer structure the viscosity of the liquid polymers depends entirely on the molecular weight produced in the controlled splitting. The viscosity varies with temperature, as shown in Figure 1. The molecular weights of the polymers have been determined by cryoscopic methods, by titration for terminal thiol groups⁴, and by measurement of the water produced on oxidation with excess lead peroxide. A suitable solvent has not as yet been found for conducting amperometric titrations⁵.

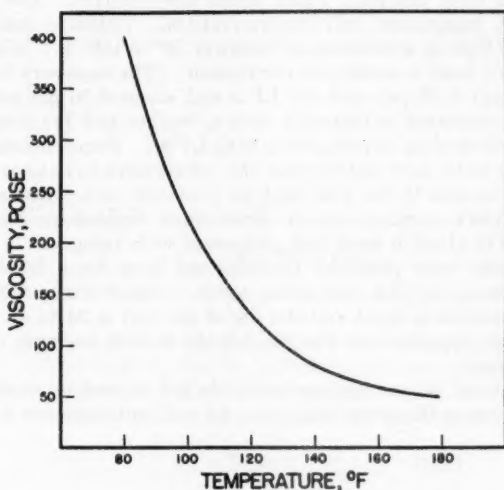


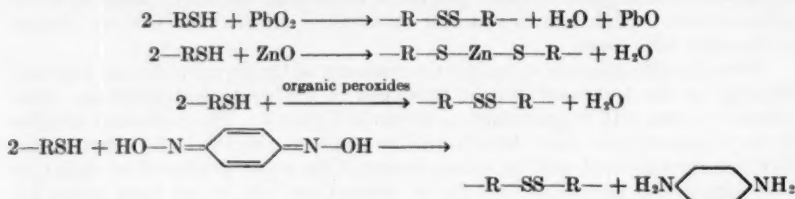
Fig. 1.—Effect of temperature on viscosity of Thiokol LP-2.

The odor of the liquid polymers produced from dichloroethyl formal is caused by the presence of low molecular-weight dithiols⁶. Because of the distribution of molecular weight species present, even the liquid polymer of highest molecular weight has some dithiols present, with high enough vapor pressure to cause odors. Conversion by oxidation to the high polymer eliminates volatile dithiols and also the odor.

VULCANIZATION

The most useful reaction for conversion of the liquid polymers to the high polymer state is that of direct oxidation. This reaction results in a linking of the two thiols to form the polymeric disulfide, with liberation of water as a byproduct. The important problems are distribution of the oxidizer in the mix and adjustment of curing aids or inhibitors to control the rate of reaction. As would be expected, alkaline environment accelerates the oxidation. Heating also accelerates the reaction and, because the reaction is exothermic, once

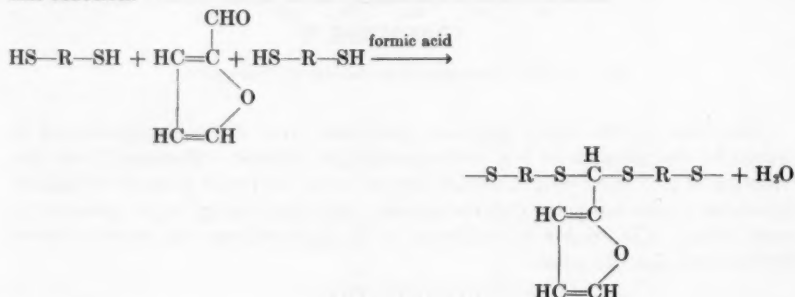
conversion has started it proceeds at a rapid rate. Typical reactions are:



In some cases where conversion is desired for films of 5 to 50 mils, the oxygen can be supplied from the air. Paint driers are effective. The most active driers are cobalt, manganese, and iron derivatives. Cobalt is outstanding and yields converted films in a temperature range of 50° to 150° F. Manganese and iron driers require heat to accelerate conversion. The necessary concentration of cobalt is about 0.25 per cent for LP-2 and about 0.50 per cent for LP-3. (LP-8 has been converted in materials such as leather and Transite by a cobalt drier solution, followed by impregnation with LP-8.) Some chelate compounds of cobalt known to be more active than the cobalt salts have been used experimentally. Conversion is too fast, and no practical formulations are known. Compositions which contain cobalt drier have limited package stability. Skinning occurs in about a week and progresses with aging.

Recently, some very practical formulations have been developed to use oxygen from the air as the converting agent. Conversion on air drying at ambient temperatures is rapid and the life of the mix is 24 to 48 hours. The formulations and properties are discussed in the section covering typical application formulations.

There are several other reactions which do not depend on oxidation. Furfural reacts to form a thioacetal linkage. An acid environment is required for this reaction.



The liquid polymers combine with phenol formaldehyde, resorcinol formaldehyde, furfuryl alcohol, epoxide, and related resins. The properties of products of combination depend on the ratio of liquid polymer to resin. The main values seem to lie in use of low concentration of resin to develop the toughness in the converted liquid polymers or to use fairly low concentrations of liquid polymers to develop flexibility in the resins.

In some conversion reactions the water content of the compound has a marked effect on the rate of conversion, as shown in Figure 2. The humidity

at which the compound is mixed and used has a similar effect on rate, as shown in Figures 3 and 4. Apparently traces of moisture act to catalyze the oxidation reaction. Because water is a normal byproduct of the reaction, the major effect on rate is noted during the induction period. Lead peroxide is particularly sensitive to the presence of moisture. To decrease the variations in rate of conversion a minimum concentration of moisture is desirable in the compound.

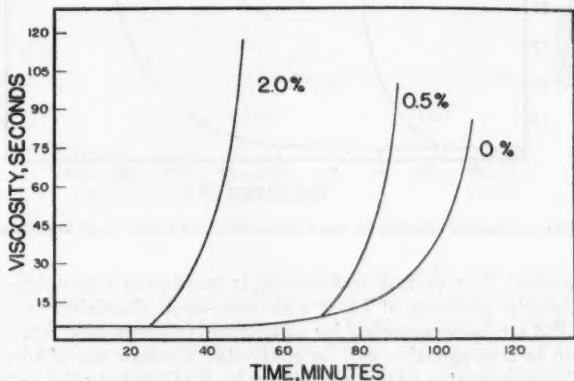


Fig. 2.—Effect of added water on rate of cure of Thiokol LP-2. Lead peroxide conversion.

For some applications it is desired to limit the ultimate molecular weight. In the case of liquid polymers, this can be controlled very easily by use of mono-functional thiol compounds. Typical compounds which have been used successfully are mercaptoethanol, xyleneethiol, and α -tolueneethiol.

COMPOUNDING

Applications where maximum fluidity is required make use of uncompounded liquid polymer. Typical examples of these are casting and impregna-

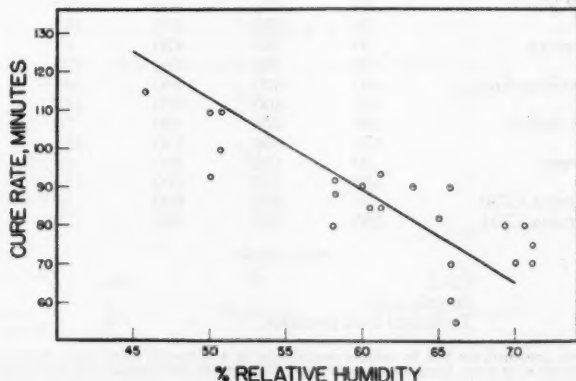


Fig. 3.—Effect of relative humidity on time of cure of Thiokol LP-2. Lead peroxide conversion.

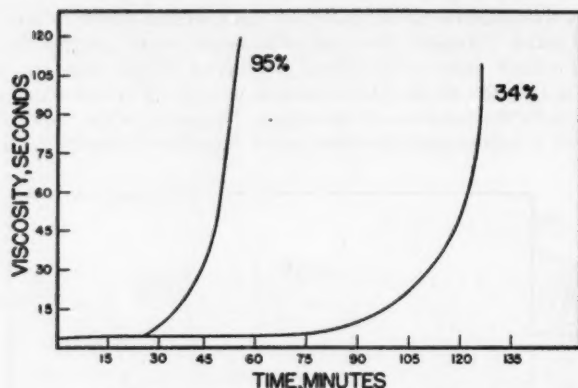


Fig. 4.—Effect of relative humidity on rate of cure of Thiokol LP-2. Lead peroxide conversion.

tion compounds. For casting compounds in particular minimum, porosity is desired. Usually mixtures of LP-2 with ester-type plasticizer or mixtures of LP-2 and LP-3 are basic materials for casting and impregnation work. Amount of deposition in impregnation can be controlled through use of solvents. For casting, either accelerator pastes containing lead peroxide as the active ingredient or organic peroxides are added just before application. There is an induction period at the start, followed by an exothermic reaction, resulting in rapid increase in viscosity and molecular weight. For good results casting must be done before initiation of the conversion reaction. It is possible to delay the reaction somewhat after converting agents are added by storage under refrigeration. Impregnation permits greater leeway. The object to be impregnated

TABLE III

EFFECT OF FILLERS ON PHYSICAL PROPERTIES OF LP-2 VULCANIZATES

Filler	Parts	Tensile strength	Elongation (%)	Tear index	Shore A hardness
SRF black	30	575	460	127	53
	50	870	470	169	61
Thermax	50	385	420	63	46
	90	790	490	226	62
Titanium dioxide	100	620	540	105	60
	150	600	570	112	70
Zinc sulfide	100	570	490	70	52
	150	600	320	155	69
Calcene	50	455	490	38	52
	100	475	590	114	63
Alumina C730	50	505	600	50	52
Alumina C741	100	390	600	79	55

Basic recipe

LP-2	100
Stearic acid	1
Technical lead peroxide	8

Samples were prepared for test by milling ingredients on a three-roll paint mill. Compounds were allowed to set 48 hours at room temperature and were then ground and pressed out in a platen press for 10 minutes at 310° F.

TABLE IV
FORMULATIONS FOR CAULKING COMPOUNDS

LP-2	100	100	100	100
Stearic acid	1	1	1	1
SRF black	30	—	—	—
Calcene	—	20	20	—
Mapico brown	—	3	—	—
Red oxide	—	2	—	—
Zinc sulfide	—	—	10	—
Titanium oxide	—	—	—	80
Accelerator C-5 ^a	15	15	15	15
Rheological properties	Fluid	Thixotropic	Thixotropic	Thixotropic
Color	Black	Red	Tan	Cream
Pot life, hours				2 to 3
Set time (80° F hours)				8 to 16
Set time (158° F hours)				1 to 2

^a Lead peroxide (90% commercial) 7.5, stearic acid 0.75, dibutyl phthalate 6.75.

—leather, for example—can be preimpregnated with a converting agent or catalyst, followed by the impregnation dip in polymer or polymer solution.

Most uses require addition of reinforcing fillers, pigments, resins, or plasticizers. Fillers both strengthen and reduce cost of compounds. Resins are used to improve adhesive properties and plasticizers are used to reduce viscosity as well as to extend compounds. The most commonly used fillers are medium thermal (MT), semireinforcing furnace (SRF), and fine furnace (FF) blacks. Several white fillers can be used, although these result in somewhat more expensive compounds. Zinc sulfide, lithopone, and titanium dioxide have been used for specific applications. Zinc oxide is a good reinforcing filler, but must be used with special attention, because it also acts as a converting agent. Neutral fillers, such as calcium carbonate and aluminum oxide, have been found useful. These fillers are not so good for reinforcing properties as those mentioned previously, but serve in some compounds as low-cost extenders (Table III).

Inert dry pigments are stirred into the liquid polymers. Dispersion of pigments in the LP-2 can be accomplished by means of a three-roll paint mill,

TABLE V
FORMULATIONS OF CASTING COMPOUNDS

LP-2	100	100	100
Stearic acid	—	1	—
Oleic acid	—	—	3.0
Dibutyl phthalate	10	—	—
Santicizer M-17 ^a	—	50	—
Tributyl citrate	—	—	30
Sulfur	0.4	—	0.5
MT black	—	100	—
Zinc sulfide ^b	50	—	—
Accelerator C-5 ^c	15	20	15
Pot life (min.)	15 to 30	4 to 6 hours	5 to 10
Set time (68° F hours)	2 to 4	24 to 48	1 to 2

^a Methyl phthalyl ethyl glycolate, Monsanto Chemical Co.

^b ZS 800, New Jersey Zinc Co.

^c Lead peroxide (90% commercial) 7.5, stearic acid 0.75, dibutyl phthalate 6.75.

TABLE VI
FORMULATIONS OF THIOKOL LP-2 ADHESIVES

LP-2	100	100
SRF black	30	—
Phenolic resin ^a	10	10
Stearic acid	1	1
Accelerator C-5 ^b	20	20
Pot life, hours	1 to 2	
Set time (68° F, hours)	8 to 16	

^a Durez 10694 or Bakelite 6741.

^b Lead peroxide (90% commercial) 7.5, stearic acid 0.75, dibutyl phthalate 6.75.

TABLE VII
FORMULATIONS OF AIR-DRYING PAINTS

	T74F	T74G
LP-2 base paint		
LP-2	100	100
Furnex	—	50
Statex-B	25	—
Sterling-105	25	—
Zinc peroxide	3	3
Toluene	—	27
Cyclohexanone	104	—
Methylethyl ketone	104	98
Accelerator B		
Sulfur	2.3	1.75
VYHH solution (20%) ^a	3.45	2.65
Accelerator C		
Diphenylguanidine	0.72	0.55
Methylethyl ketone	2.88	2.20

Physical properties

	T74F	T74G
Tensile strength (lb./sq. inch)	1400	900
Elongation (%)	550	275
Hardness (Shore Type A)	60	60
Tear index (Winkelmann)	320	150
Compression set ^b	50%	—
Low temperature flexibility	O.K. at -65° F	O.K. at -65° F
Heat stability (1 week at 250° F)	O.K.	O.K.
SR-6 fuel extraction ^c	5% loss	5% loss
Sea water (2 years' immersion)	No change	No change
Pot life, hours	24 to 48	
Tack free, hours	2 to 4	
Cure time (10 mils) (day)	1	
Cure time (50 mils) (days)	5	

^a Vinylite VYHH dissolved in methylethyl ketone.

^b A.S.T.M. D 395-49T, 2 hours at 158° F.

^c Apparatus as an A.S.T.M. D297-43T, 20 hours' refluxing.

a ball mill, or an internal mixer. The type of compound required generally determines the most suitable mixing device. The conversion accelerator is prepared as a separate mix. Lead peroxide can be dispersed in dibutyl phthalate, with a small amount of stearic acid to prevent rapid settling and caking of

the lead peroxide. The organic peroxides which are used are soluble in the polymers and can be added as supplied or in diluted form.

One of the important uses for liquid polymers has been in caulking compounds which can be applied by means of a trowel or gun. The compounds shown in Table IV are intermediate in cure rate properties. Compounds can be adjusted to convert in less than 1 hour and, by varying the accelerator or oxidizer used, conversion can be retarded so that heating at 150° to 200° F is required.

Casting compounds are designed for low viscosity. Only a minimum of thixotropy can be tolerated, or the resultant products will have excessive porosity. Highly plasticized compounds have poor physical properties, but in many applications the compound is supported or contained and tensile strength properties are of relatively little importance (Table V).

An interesting application for low viscosity compounds is in making plugs in electrical cables. The basic polymer has good electrical properties; volume-resistivity 5×10^{10} ohms per cm., power factor 0.0410, and dielectric constant 7.50.

Compounds can be used as cold setting adhesives for bonding glass, wood, and metals. Solvent cleaning is adequate for furnace preparation. Typical compounds are shown in Table VI.

TABLE VIII

SOLVENT RESISTANCE OF AIR-DRYING PAINTS

Solvent	Volume swell ^a , %
SR-6 fuel	10
SR-10 fuel	0
Acetone	30
Methylethyl ketone	50
Ethyl acetate	45
Carbon tetrachloride	60
Ethyl alcohol	0
Water	3

^a 1 month at 80° F.

TABLE IX

CHEMICAL RESISTANCE OF AIR-DRYING PAINTS

Chemical	Appearance
Ammonium hydroxide, concd.	O.K.
Sodium hydroxide	
10%	O.K.
50%	O.K.
Aluminum sulfate, satd.	O.K.
Sodium carbonate, satd.	O.K.
Sodium chloride, satd.	O.K.
Formaldehyde, 37%	O.K.
Hydrochloric acid	
10%	O.K.
30%	Fair
Sulfuric acid	
20%	Fair
60%	Bad
Nitric acid, 20%	Bad

^a 2 months' immersion at 80° F.

One important use for liquid polymers is impregnation of porous materials, followed by conversion in place to a rubber of high molecular weight. This method has been successful for filling voids in leather⁷, wood, felt, fabric, Transite, and porous castings.

The following examples listed show the methods used in impregnating leather.

HEXOGEN COBALT (2 PER CENT) PREIMPREGNATION

1. 10-min. dip in cobalt solution in toluene
2. 30-min. drying to allow solvent evaporation
3. 1-hour drying at 158° F to drive out residual solvent
4. 30-min. dip in 50% solution of LP-2^a

CUMENE HYDROPEROXIDE-TRIPHENYLGUANIDINE CURE

1. 10-min. in 5% triphenylguanidine in methylethyl ketone
2. 30-min. drying at room temperature
3. 1-hour forced drying at 158° F
4. 30-min. dip in

LP-2

Solvent^a

Cumene hydroperoxide^b

100

100

7

^a 50/50 toluene-methylethyl ketone.

^b 70% solution.

Air-drying coatings are one of the most recent developments, and promise to be of considerable value to the consumer market in addition to industrial applications. The formulations are prepared at high solids (40 to 60 per cent) and can be applied by brushing, spraying, or dipping. They are adjusted to paint viscosity and behave much like paints containing drying oils. Conversion takes place at ambient temperatures and depends on oxygen from the air as the main vulcanizing agent. A combination of catalysts is used to promote the conversion.

The film is serviceable over a wide temperature range (-65° to +250° F) and has excellent ozone, weathering, and solvent resistance. A novel characteristic of this paint is that it can be applied in one coat to any desired thickness up to 50 mils without flow even on vertical surfaces.

This paint is now being investigated as a protective coating over wood, steel, aluminum, magnesium, and natural rubber. To develop a bond, it is recommended that a primer be used on the surface to be coated⁸.

The liquid polymers were developed and promoted for several service applications during World War II, but no effort was made to apply them to industrial problems until termination of hostilities. During the past five years, many established uses have developed for which the polymers have proved satisfactory. The major outlet for compounds is in cabin sealing and sealing integral fuel tanks in aircraft. However, considerable quantities are used in leather impregnation and in the preparation of flexible molds. Several problems in the preservation of ships were answered through the use of LP-2 compounds.

The number of different liquid polymers which can be produced is unlimited. The products which are now manufactured can be adapted by compounding techniques to extend the fields of application. Special polymers can be prepared to meet application conditions which cannot be filled by present materials.

ACKNOWLEDGMENT

The authors are indebted to the laboratory staffs of the Development and Technical Service Departments, who obtained much of the information upon which this articles is based.

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- ⁸ Suitable primers are EC-853 and EC-776 (Minnesota Mining & Manufacturing Co., Adhesives Division).





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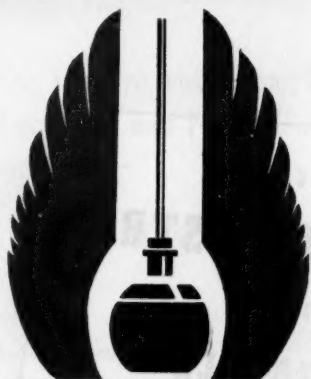
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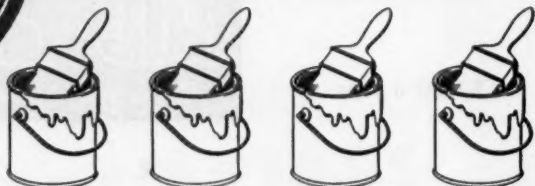
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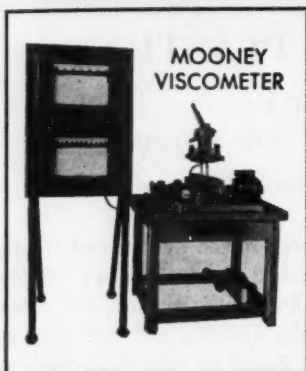
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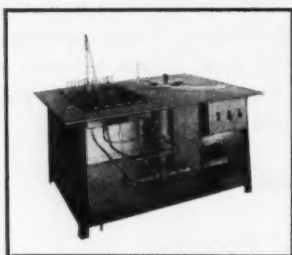
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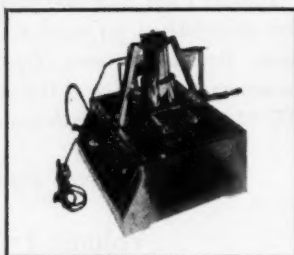
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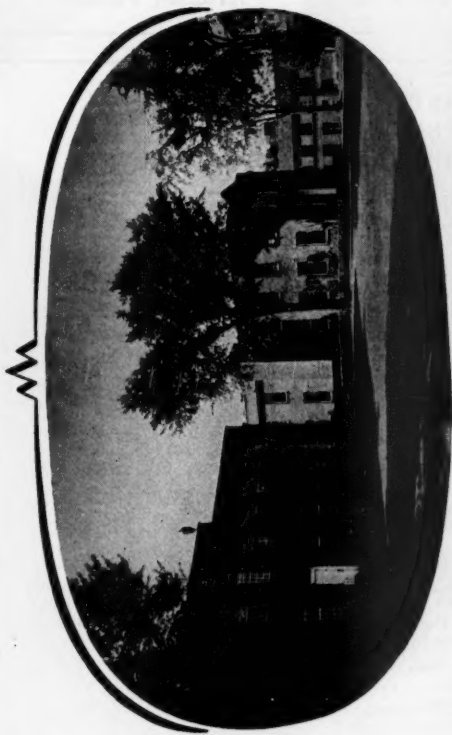
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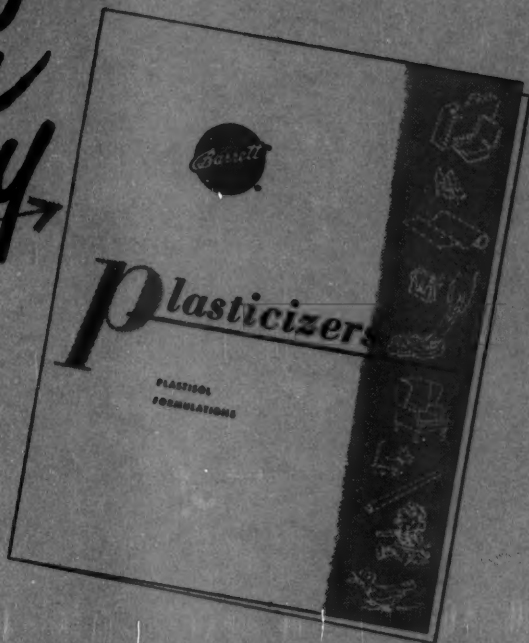
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New Surface Area Values for HORSE HEAD ZINC OXIDES

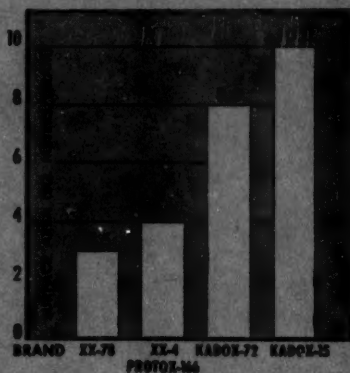
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*Brenauer, Emmett and Teller, J. Amer. Chem. Soc. 60, 309 (1938).

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